

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244992943>

The Effect of Charge of Polymeric Stabilizing Agents on the Quantum Yield of Photoinduced Electron Transfer from Photoexcited Colloidal Semiconductors to Adsorbed Viologens:

DATASET · JULY 2013

READS

13

Effect of Charge of Polymeric Stabilizing Agents on the Quantum Yields of Photoinduced Electron Transfer from Photoexcited Colloidal Semiconductors to Adsorbed Viologens

Yoshio Nosaka^{†*} and Marye Anne Fox^{*†}

Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, and
Department of Chemistry, Technological University of Nagaoka, Nagaoka 940-21, Japan

Received May 4, 1987. In Final Form: July 6, 1987

Colloidal CdS particles stabilized with several charged and uncharged polymers were excited by a laser pulse and the quantum yields Φ for the reduction of surface-adsorbed methylviologen or (sulfonatopropyl)viologen were measured. The ionic charge of the stabilizing agent, which enveloped the particle by a Langmuir-type adsorption equilibrium, influenced Φ but not the observed interfacial electron transfer rates.

Introduction

Interfacial electron transfer occurring at solid semiconductor-liquid electrolyte junctions is important in understanding their utility as photocatalysts.¹⁻³ Colloidal semiconductor sols are convenient for investigating the detailed mechanisms of primary photophysical processes occurring on these optically transparent species. Recently, we have reported the quantum yield for the reduction of methylviologen on irradiated colloidal CdS particles and the quantitative dependence of Φ on incident light intensity.⁴ In our previous study, polyacrylic acid (PAA) was used as a stabilizing agent for the colloid. Since the stabilizing polymer which surrounds the colloidal semiconductor particle is expected to have a role parallel to that assumed by coatings in polymer-modified electrodes, we have investigated the role of the stabilizing agent on interfacial electron transfer reactions on colloidal semiconductor particles.

Using the zwitterionic (sulfonatopropyl)viologen (SPV⁰) and dicationic methylviologen (MV²⁺) as electron acceptors in steady-state irradiation experiments, Thomas et al. found that electrostatic interaction between electron acceptors and stabilizing surfactants influences the yield of viologen cation radical.^{5,6} However, a systematic and quantitative investigation of this effect has not yet been reported. With colloidal TiO₂, Graetzel et al.^{7,8} investigated the kinetics of interfacial transfer of conduction band electrons. Although it is well-known that viologens adsorb on colloidal CdS particles,^{9,10} no adsorption on TiO₂ has been reported except with polymeric viologens.¹¹

In the present study, however, by using low-intensity laser pulses, we can characterize kinetically the fast electron transfer from colloidal TiO₂ to viologens, which we assume to be surface-adsorbed, as has been established with colloidal CdS. Thus, the effect of surface charge of the colloidal TiO₂ particle as well as that of the polymeric stabilization agent can be investigated by measuring the electron transfer quantum yield induced by the laser pulse.

Experimental Section

Cadmium nitrate (Cd(NO₃)₂), sodium sulfide (Na₂S·9H₂O), 1,1'-dimethyl-4,4'-dipyridinium dichloride (methylviologen, MV²⁺), benzophenone, naphthalene, poly(acrylic acid) (PAA) (Aldrich Chemical Co.), tetraisopropyltitanate, sodium hexametaphosphate (HMP) (Alfa Products), poly(vinyl alcohol) (PVA) (Sigma Chemical Co.), poly(ethyleneimine) (PEI), and poly(diallyldi-

methyammonium chloride) (PDA) (Polysciences, Inc.) were used as received. 1,1'-Bis(propylsulfonato)-4,4'-bipyridinium ((sulfonatopropyl)viologen, SPV⁰) was synthesized by mixing dry 4,4'-bipyridine and 1,3-propanesultone (Aldrich) in ethanol and was purified by recrystallization from an ethanol-water mixture.¹² At the pH of our experiment, PAA and hexametaphosphate are polyanionic, PVA and PEI are neutral, and PDA is polycationic.

Colloidal CdS stabilized with PAA was prepared by injecting a deaerated 0.5-mL aqueous solution of 10 mM Cd(NO₃)₂ into a deaerated solution containing 1 mM Na₂S and 0.02 wt % PAA. Colloidal CdS stabilized with the other agents was prepared as follows: A 6-mL solution containing 0.018 wt % stabilizing agent and 0.9 mM Cd(NO₃)₂ was bubbled with N₂ gas to remove oxygen. Into this solution, H₂S gas was injected until the color formation had ceased. N₂ gas was then bubbled through the reaction mixture in order to remove excess H₂S.

Absorption thresholds around 490 nm were observed for each CdS colloidal sol. Thus, the polymeric stabilizer did not cause appreciable variation in particle size. According to reports by Henglein¹³ and Brus,¹⁴ this absorption edge corresponds to an average particle diameter of less than 10 nm. Since the colloidal particles are very small compared to the excitation wavelength, light scattering is negligible.

Colloidal TiO₂ was prepared by the method of Graetzel et al.⁸ and Albery et al.¹⁵ One-half milliliter of a 5% 2-propanol solution of tetraisopropyltitanate was injected into 4.5 mL of 0.05 M aqueous HClO₄. The resulting solution was then bubbled with

(1) *Organic Phototransformations in Nonhomogeneous Media*; Fox, M. A., Ed.; ACS Symposium Series 278; American Chemical Society: Washington, DC, 1985.

(2) *Homogeneous and Heterogeneous Photocatalysis*; Pelizzetti, E., Serpone, N., Eds.; NATO ASI Series, Series C, No. 174; Reidel: Dordrecht, 1986.

(3) Kalyanasundaram, K.; Graetzel, M.; Pelizzetti, E. *Coord. Chem. Rev.* 1986, 69, 57.

(4) Nosaka, Y.; Fox, M. A. *J. Phys. Chem.* 1986, 90, 6521.

(5) Kuczyński, J.; Thomas, J. K. *J. Phys. Chem.* 1983, 87, 5498.

(6) Kuczyński, J.; Thomas, J. K. *Langmuir* 1985, 1, 158.

(7) Graetzel, M.; Frank, A. J. *J. Phys. Chem.* 1982, 86, 2964.

(8) Duanghong, D.; Ramsden, J.; Graetzel, M. *J. Am. Chem. Soc.* 1982, 104, 2977.

(9) Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* 1982, 86, 2291.

(10) Serpone, N.; Sharma, D. K.; Jamieson, M. A.; Graetzel, M.; Ramsden, J. *Chem. Phys. Lett.* 1985, 115, 473.

(11) Nakahira, T.; Graetzel, M. *J. Phys. Chem.* 1984, 88, 4006.

(12) (a) Willner, I.; Ford, W. E. *J. Heterocycl. Chem.* 1983, 20, 1113. (b) Nagamura, T.; Kurihara, T.; Matsuo, T. *J. Phys. Chem.* 1982, 86, 4368.

(13) Weller, H.; Schmidt, H. M.; Koch, U.; Fojtik, A.; Baral, S.; Henglein, A.; Kunath, A.; Weiss, K.; Dieman, E. *Chem. Phys. Lett.* 1986, 124, 557.

(14) Rossetti, R.; Ellison, L. J.; Gibson, J. M.; Brus, L. E. *J. Chem. Phys.* 1984, 80, 4464.

(15) Albery, W. J.; Bartlett, P. W.; Porter, J. D. *J. Electrochem. Soc.* 1984, 131, 2896.

[†] University of Texas at Austin.

^{*} Technological University of Nagaoka.

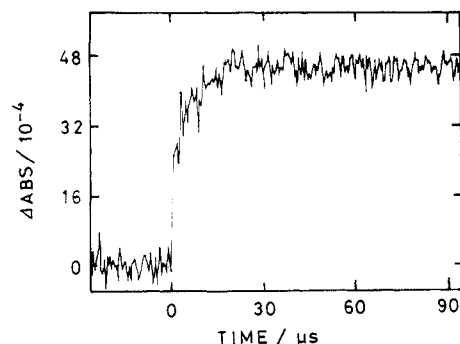


Figure 1. Time profile of the 606-nm absorption of MV^{+} after laser pulse excitation. The absorbance of TiO_2 at the excitation wavelength was 0.36 cm^{-1} , $[MV^{2+}] = 10\text{ mM}$, $[\text{photon}] = 3.3\text{ }\mu\text{M}$.

N_2 for a few hours. The clear TiO_2 sol was mixed with 5 mL of 0.2 wt % PVA solution and then deionized with Amberlite MB-3A. The final pH of the TiO_2 /PVA sol was 6.0.

Pulse laser transient absorption measurements were performed at the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. Samples were prepared in 5 mm \times 10 mm quartz cells by mixing the colloidal sol with deaerated water containing a desired amount of the viologen under a nitrogen atmosphere. The third harmonic beam (355 nm) of a Q-switched Nd:YAG laser (Quantel YG-581 and YG-481, pulse duration (Δt) = 10 ns) was used. The analyzing light from a 150-W Xe lamp source equipped with a pulse intensifier (Photochemical Research Associates, Inc.) passed through a 550-nm cut-off filter and was focused onto a 0.5-mm round aperture located at a 10-mm side of the sample cell. The 5-mm side of the sample cell was irradiated with the laser pulse, which was attenuated with glass filters and a set of polarizers. The light intensity of the laser pulse was measured by observing the intensity of the transient absorption of the naphthalene triplet produced by benzophenone sensitization in a deaerated hexane solution.¹⁶ In the actinometer, the concentration of naphthalene was 0.1 M and that of benzophenone was adjusted to have the same absorbance in each colloidal sol ($0.4\text{--}1.0\text{ cm}^{-1}$). From the known triplet quantum yield, the incident light intensity could be calculated directly. In order to express the laser intensity, the observed concentration of absorbed photons was normalized to 0.2 cm^{-1} absorbance and is referred to as a concentration of photons. From a simple calculation, it can be estimated that the laser intensity required to produce a $[\text{photon}] = 1\text{ }\mu\text{M}$ corresponds to a photon flux of $1.3 \times 10^{16}\text{ photons/cm}^2$ or an energy flux of 0.7 mJ/cm^2 at 355 nm. Since the extinction coefficient of reduced methylviologen is known, a determination of the intensity of the transient absorption provides a direct measure of the quantum efficiency of its formation. Data derived for each sample were recorded for more than five laser shots and were treated by using previously described analysis programs.¹⁷ Absorption spectra were measured with a Hewlett-Packard 8450 spectrophotometer.

Results and Discussion

Upon excitation of colloidal CdS in the presence of adsorbed viologen by the laser pulse, a transient absorption at 606 nm, attributable to the singly reduced viologen cation radical, was produced without time delay. This observation was a common feature for each colloidal CdS, irrespective of the protective agent or the adsorbed viologen.^{9,10,18,19}

Figure 1 represents the temporal absorption changes observed at 606 nm (assigned as reduced viologen) after pulse irradiation of the colloidal TiO_2 sol containing 10 mM MV^{2+} . The time profile consists of a fast rise immediately after the laser pulse and a slow growth on the microsecond

Table I. Photophysical Parameters for Interfacial Electron Transfer on Irradiated Colloids Stabilized by Polymers^a

colloid	pH	viologen	Φ_0	K_{app}/M^{-1}	$(k_r/k_e)/10^{-19}\text{ cm}^3$
CdS/PAA	10	MV^{2+}	0.117	17200	6.6
		SPV^0	0.062	90	
CdS/PDA	7.1	MV^{2+}	0.051	49	20
		SPV^0	0.063	285	
CdS/PEI	12	MV^{2+}	0.127	82	4.4
		SPV^0	0.076	86	
CdS/PEI	5.5	MV^{2+}	0.174	30	16
		SPV^0	0.246	500	12
CdS/HMP	7.0	MV^{2+}	0.046	10000	
		SPV^0	0.193	7400	3.9
TiO_2 /PVA	6.0	MV^{2+}	0.072	700	
		SPV^0	0.068	40	

^a Photoinduced electron-transfer quantum yields at infinite concentration (Φ_0) for charged and uncharged viologens, apparent association constants (K_{app}) obtained from eq 1, and kinetic parameters obtained from eq 2.

time scale. Although Graetzel et al.^{7,8} have already reported the slower growth of the MV^{+} radical, they did not mention the fast rise. The component responsible for the fast rise seems to be too small to observe at higher laser intensities. The observed slow growth probably corresponds to electron transfer from the conduction band to viologen in the bulk solution^{8,20} or to reduction by radicals formed in the scavenging of holes,²¹ while the fast rise can reasonably be assigned to an immediate reduction of surface adsorbed MV^{2+} . Since the slow growth has been analyzed by Graetzel et al.⁸ and by Darwent et al.,²⁰ we describe, in the present study, electron transfer only to adsorbed viologen. Hole transfer on aqueous colloidal sols is much slower than electron transfer to adsorbed viologen, although the photogenerated hole may participate in back electron transfer.

With colloidal CdS stabilized with ionic polymers, the quantum yield Φ for electron transfer to viologens having different charges was measured. The value of Φ obtained at the time immediately after the laser pulse was calculated from the absorption at 606 nm for MV^{+} ($\epsilon = 13\,700\text{ M}^{-1}\text{ cm}^{-1}$)²² and at 602 nm for SPV^{+} ($\epsilon = 12\,800\text{ M}^{-1}\text{ cm}^{-1}$).²³ The Φ values obtained are shown in Figure 2, together with the initial concentration of viologen.

The solid curves in Figure 2 are calculated fits for the data points obtained by assuming a Langmuir adsorption equilibrium for the viologen on the colloidal particle where

$$\Phi = \Phi_0 K_{app}[\text{viologen}]/(1 + K_{app}[\text{viologen}]) \quad (1)$$

K_{app} is an apparent association constant and Φ_0 is the electron transfer quantum yield at infinite viologen concentration. A similar relationship has been reported for the adsorption of thionine²⁴ or SCN^{-25} on colloidal TiO_2 . The values for K_{app} and Φ_0 obtained by curve fitting for each of the colloid/stabilizer systems are listed in Table I. pH values of the resultant colloidal suspension are also included in the table.

With CdS/PAA (Figure 2a), the value of the quantum yield of cationic MV^{2+} reaches the maximum at very small concentrations of viologen, while that for neutral, zwitterionic SPV^0 shows a weaker concentration dependence.

(20) Brown, G. T.; Darwent, J. R. *J. Chem. Soc., Chem. Commun.* 1985, 98.

(21) Bahnemann, D.; Henglein, A.; Lilie, J.; Spanhel, L. *J. Phys. Chem.* 1984, 88, 709.

(22) Watanabe, T.; Honda, K. *J. Phys. Chem.* 1982, 86, 2617.

(23) Willner, I.; Yang, J.-M.; Laane, C.; Otvás, J. W.; Calvin, M. J. *Phys. Chem.* 1981, 85, 3277.

(24) Kamat, P. V. *J. Photochem.* 1985, 28, 513.

(25) Kamat, P. V. *Langmuir* 1985, 1, 608.

(16) Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* 1971, 67, 1904.

(17) Foyt, D. C. *Comput. Chem.* 1981, 5, 49.

(18) Kuczyński, J.; Thomas, J. K. *Phys. Chem. Lett.* 1982, 88, 445.

(19) Rossetti, R.; Brus, L. E. *J. Phys. Chem.* 1986, 90, 558.

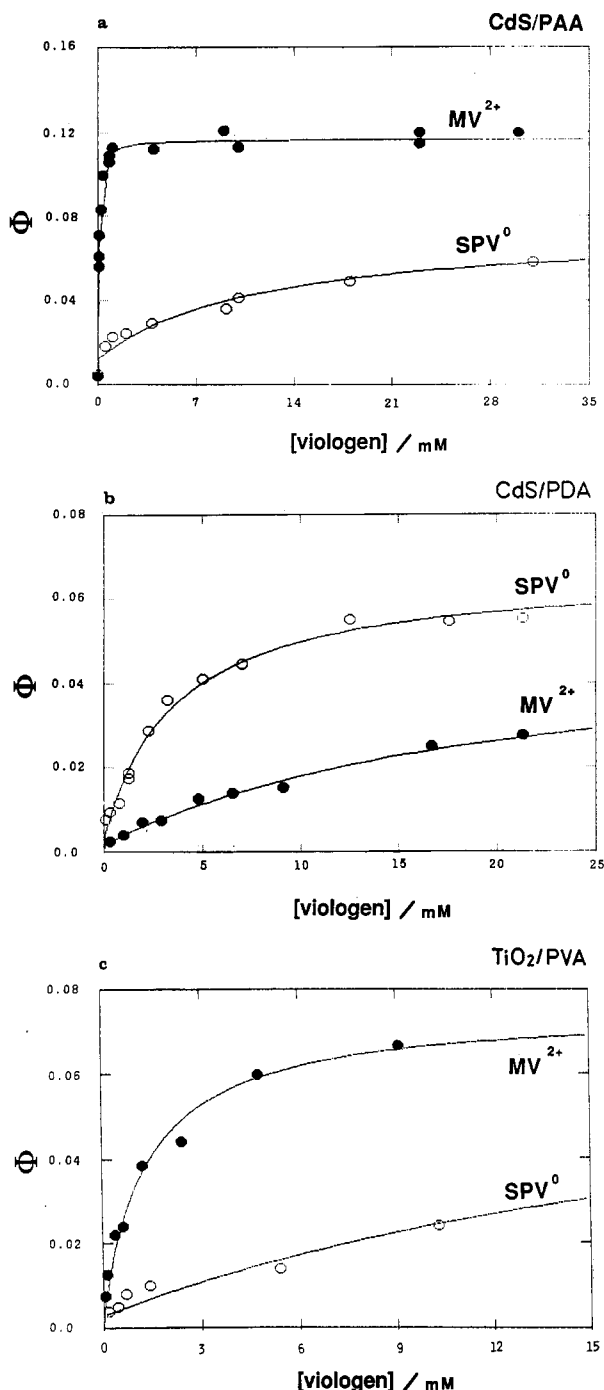


Figure 2. Quantum yield Φ for the reduction of charged and uncharged viologens immediately after a 355-nm laser pulse as a function of initial viologen concentration: (a) colloidal CdS stabilized with anionic polymer PAA, absorbance at 355 nm was 0.6–0.8 cm^{-1} , [photon] = 5.5 μM ; (b) colloidal CdS stabilized with cationic polymer PDA, absorbance at 355 nm was 0.55–0.65 cm^{-1} , [photon] = 3.0 μM ; (c) colloidal TiO_2 stabilized with nonionic polymer PVA, pH 6.0, absorbance at 355 nm was 0.5–1.0 cm^{-1} , [photon] = 2.6 μM .

This contrasting behavior clearly requires a strong ionic attractive interaction between the carboxylate groups of PAA and the quaternary nitrogen of MV^{2+} . In Figure 2b, the quantum yield for the CdS colloid stabilized with poly(diallyldimethylammonium) (PDA) is shown. In this case, the more modest increase of Φ with initial MV^{2+} concentration can be attributed to repulsive electrostatic interactions with the cationic ammonium groups of PDA. For TiO_2 colloids stabilized with nonionic poly(vinyl alcohol) (PVA), the quantum yield immediately after the

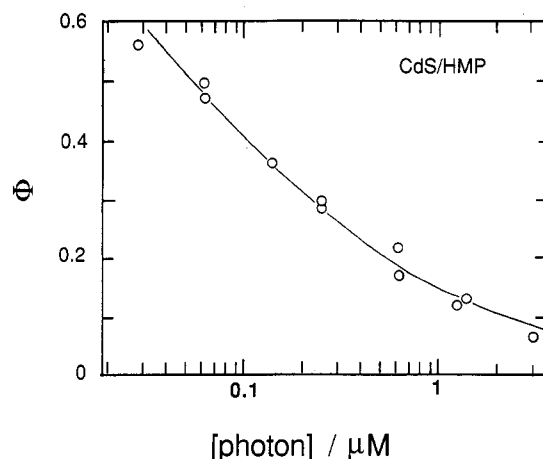


Figure 3. Quantum yield of the reduction of (sulfonatopropyl)viologen (SPV^0) on CdS stabilized by hexametaphosphate as a function of the laser pulse intensity. [SPV^0] = 2 mM. The curve is calculated from eq 2 by adopting $K\epsilon = 9.6 \times 10^{20} \text{ M}^{-1} \text{ cm}^{-3}$ and $k_r/k_e = 3.9 \times 10^{-20} \text{ cm}^3$.

laser pulse is shown in Figure 2c, along with the initial viologen concentration. Although the stabilizing agent is nonionic, the polar colloidal TiO_2 surface^{8,20} apparently induces a larger association constant with cationic MV^{2+} . With CdS/PEI, the difference in K_{app} for MV^{2+} and SPV^0 at pH 5.5 can be explained by the partial ionization of the imine group at low pH.

We have reported previously the effect of light intensity on the electron transfer quantum yield for CdS/PAA containing MV^{2+} .⁴ When the lifetime of a photogenerated conduction band electron, $1/k_e$, is shorter than the width of the laser excitation pulse, Δt , the relationship between laser intensity (expressed as photon concentration) and Φ is given as

$$(1 - \Phi)/\Phi^2 = K\epsilon[\text{photon}]k_r/k_e \quad (2)$$

where K is a numerical constant when the lifetime of the valence band hole is longer than Δt , ϵ is the molar absorption coefficient of colloidal CdS at the excitation wavelength, and k_r is the rate constant for photoinduced electron-hole recombination. With Φ measured at various laser intensities, the rate parameter k_r/k_e can be estimated from eq 2. The typical laser-intensity dependence for the CdS/HMP sol containing SPV^0 is shown in Figure 3. The values of k_r/k_e calculated are shown in the last column of Table I. High K_{app} values are observed with colloids stabilized by anionic polymers (PAA and HMP). Although the calculation procedure for k_r/k_e assumes similar particle sizes for colloids stabilized by the various polymeric agents, the value obtained is of the same order of magnitude as that obtained by the mathematical curve fitting. This observation and the fact that the values of Φ_0 range from 0.05 to 0.25 lead to the conclusion that the efficiency of net electron transfer is not controlled by variation in the forward or reverse electron transfer rates but rather by the ionic binding of viologen with the surrounding stabilizing agent or solid surface, a conclusion which has parallel in a very recent study of charge separation on TiO_2 -modified silica.²⁶

Acknowledgment. The authors are thankful to the Japan Society for the Promotion of Science for partial fellowship support for Y.N. in the U.S. Support of this work from the U.S. Department of Energy, Basic Energy

(26) Frank, A. J.; Willner, I.; Goren, Z.; Degani, Y. *J. Am. Chem. Soc.* 1987, 109, 3568.

Sciences, Fundamental Interactions Branch, is also gratefully acknowledged. The use of the equipment at the Center for Fast Kinetics Research, a facility supported by the National Institutes of Health and by the University

of Texas at Austin, is greatly appreciated.

Registry No. MV²⁺, 4685-14-7; SPV⁰, 77951-49-6; PAA, 9003-01-4; PDA, 26062-79-3; PEI, 9002-98-6; PVA, 9002-89-5; CdS, 1306-23-6; TiO₂, 13463-67-7.

Intensity Enhancement of Infrared Attenuated Total Reflection Spectra of Stearic Acid Langmuir-Blodgett Monolayers with Evaporated Silver Island Films

Toshihide Kamata, Akira Kato, Junzo Umemura, and Tohru Takenaka*

Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan

Received May 28, 1987. In Final Form: August 31, 1987

Band intensity enhancement of infrared spectra of stearic acid Langmuir-Blodgett (LB) monolayers with evaporated Ag islands was studied by using the attenuated total reflection (ATR) technique. In the case of a one-monolayer LB film, all stearic acids react with Ag forming silver stearate. The symmetric COO⁻ stretching band, the transition moment of which is perpendicular to the Ag surface, is enhanced most. Polarization measurements of the ATR spectra and examination of the grazing incidence reflection-absorption spectra and the normal incidence transmission spectra of the stearic acid monolayers reveal that only the in-plane component of the electric field in the Ag film can enhance infrared absorptions of the monolayer. This fact is consistent with the intensity enhancement due to the high electromagnetic field due to collective electron resonances associated with the island nature of the thin metal films. In the case of multilayer LB films, the intensity enhancement decreases very rapidly with an increasing number of monolayers. This fact indicates that the effect is most prominent for the vibration bands of stearate ions directly attached to the Ag surface and that it has a long range nature of at least one molecular length, showing the enhancement is electromagnetic in nature.

Introduction

In a previous work,¹ we studied Fourier transform infrared (FTIR) attenuated total reflection (ATR) spectra of Langmuir-Blodgett (LB) films of stearic acid with one to nine monolayers. It was found that the lower limit of detection by the FTIR-ATR technique was at a level of the band intensity from the single monolayer films. Therefore, an improvement of the sensitivity of this technique is necessary for obtaining more reliable infrared spectra of these thin films.

In recent years, considerable attention has been paid to the high electromagnetic field of surface plasmon polariton (SPP) in relation to the mechanism of surface enhanced Raman scattering (SERS).² Recently, Hartstein et al.³ and Hatta et al.⁴⁻⁷ reported that the infrared absorption from organic molecules was 1 or 2 orders of magnitude enhanced by the presence of thin metal overlayers or underlayers in the ATR technique. This effect was interpreted by an electric field enhancement due to SPP or collective electron resonances associated with the island nature of the thin metal films.⁸ Furthermore, Hatta et al.⁴ observed intensity enhancement of ATR spectra of a stearic acid monolayer due to a 5-nm Ag underlayer. Sigarev and Yakovlev⁹ studied an effect of thin Ag overlayers on the ATR band intensity of mixed LB films of stearic acid and barium stearate. However, their observations were limited in the CH stretching region. In order to have more detailed information of this phenomenon, we observed the intensity enhancement of ATR spectra in the wider frequency range from 4000 to 800 cm⁻¹ of the stearic

acid LB monolayers with evaporated thin Ag films.

Experimental Section

The stearic acid used in this study is the same as that reported on previously.¹ Water was purified with a modified Mitamura Riken Model PLS-DFR automatic lab still consisting of a reverse osmosis module, an ion-exchange column, and a double distiller.

The stearic acid monolayers were transferred from the water surface onto a Ge ATR plate (Figure 1) by the LB method¹⁰ in the same way as that described previously.¹ The surface pressure of the monolayer transfer was 20 mN m⁻¹. The Ge plate was pulled down and up through the monolayer at a rate of 11 mm min⁻¹. The transfer ratios were 0.97 ± 0.03 throughout the experiments. Prior to the monolayer transfer, the Ge plate was carefully polished by using diamond pastes with particles of 1- and 0.25-μm diameters and then successively ultrasonicated in ethanol, benzene, chloroform, and distilled water for 10 min each. Finally, it was subjected to air plasma cleaning (a Harrick Model PDC-23G) at 0.1 Torr for 10 min.

The Ag films with average thickness from 0.5 to 5 nm were deposited on one large face of the Ge plate with stearic acid

- (1) Kimura, F.; Umemura, J.; Takenaka, T. *Langmuir* 1986, 2, 96.
- (2) Chang, R. K.; Furtak, T. E. *Surface Enhanced Raman Scattering*; Plenum: New York, 1982.
- (3) Hartstein, A.; Kirtley, J. R.; Tsang, J. C. *Phys. Rev. Lett.* 1980, 45, 201.
- (4) Hatta, A.; Ohshima, T.; Suetaka, W. *Appl. Phys. A* 1982, A29, 71.
- (5) Hatta, A.; Suzuki, Y.; Suetaka, W. *Appl. Phys. A* 1984, A35, 135.
- (6) Hatta, A.; Chiba, Y.; Suetaka, W. *Surf. Sci.* 1985, 158, 616.
- (7) Osawa, M.; Kuramitsu, M.; Hatta, A.; Suetaka, W.; Seki, H. *Surf. Sci.* 1986, 175, L787.
- (8) Moskovits, M. *J. Chem. Phys.* 1978, 69, 4159.
- (9) Sigarev, A. A.; Yakovlev, V. A. *Opt. Spectrosc. (Engl. Transl.)* 1984, 56, 336.
- (10) Blodgett, K. B.; Langmuir, I. *Phys. Rev.* 1937, 51, 964.

* Author to whom all correspondence should be addressed.