High Pressure Effects on Fluorescence-Quenching of Coumarin 343 Adsorbed on TiO_2 Nanocrystallites in Methanol and in *N,N*-Dimethylformamide

Masamitsu Matsumoto, Kei Murakoshi,[#] Yuji Wada, and Shozo Yanagida*
Graduate School of Material and Life Sciences, Osaka University, Yamadaoka, Suita, Osaka 565-0871

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The effect of high pressures up to 400 MPa on the emission quenching of Coumarin 343 (C343) adsorbed on TiO_2 nanocrystallites in methanol (MeOH) and *N,N*-dimethylformamide (DMF) solution was investigated. In MeOH, the quenching efficiency decreased as the pressure increased. This decrease was explained by the decrease of the adsorption strength of C343 onto TiO_2 nanocrystallites. On the contrary, the efficiency in DMF increased with increase of pressure in spite of decrease of adsorption strength of C343 onto TiO_2 under the high pressure condition, indicating enhancement in the electron transfer efficiency. The results imply that the high pressure technique can control the efficiency of photo-induced electron transfer systems.

Improvements of dye-sensitization efficiency are one of the most important subjects related to solar-energy conversion.[1] Control of the coupling between the dye and semiconductor surface is one of the difficult problems in the construction of the system. We have pointed out that formation of specific binding structure has an important role for photo-induced electron transfer.[2] Incidentally, the pressure effect has been reported to be one of the operational environmental parameters of liquid phase reactions.[3] Under the high pressure condition, more effective adsorption of aromatic compounds [4] and solvents [5] onto solid surfaces has been investigated. The electron transfer mechanism of the dye-sensitized TiO_2 photoanode was discussed using photocurrent spectrum under high pressure.[6] These studies promoted us to investigate the pressure effect on the system of dye-sensitization.

A homogeneous solution of dye-adsorbed TiO_2 nanocrystallites is transparent and gives a model of a dye sensitizing system. When C343 is adsorbed on TiO_2 nanocrystallites, the peak of the dye absorption shifts to longer wavelength by ca. 20 nm, its absorbance increases, and the luminescence of the dye is quenched effectively.[7] This quenching is attributed to the electron transfer to the conduction band of TiO_2 nanocrystallites from the excited dye molecules.

In this letter, we aimed to clarify the high-pressure effect on the dye sensitizing system. Absorption and emission spectra of C343 adsorbed on TiO_2 nanocrystallites in MeOH and DMF were measured under the high pressure conditions up to 400 MPa.

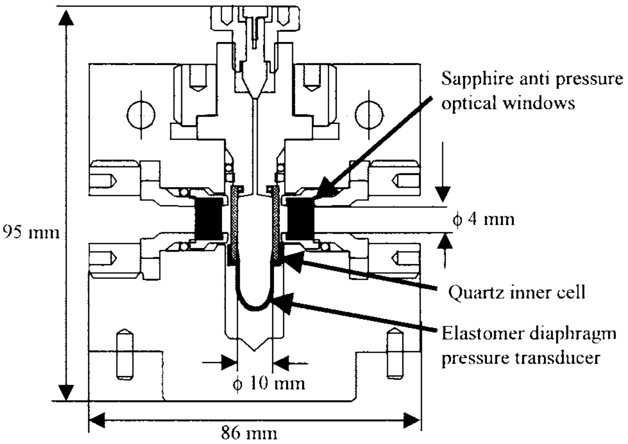

Figure 1. High Pressure Optical Cell equipped into a sample chamber of a spectrophotometer.

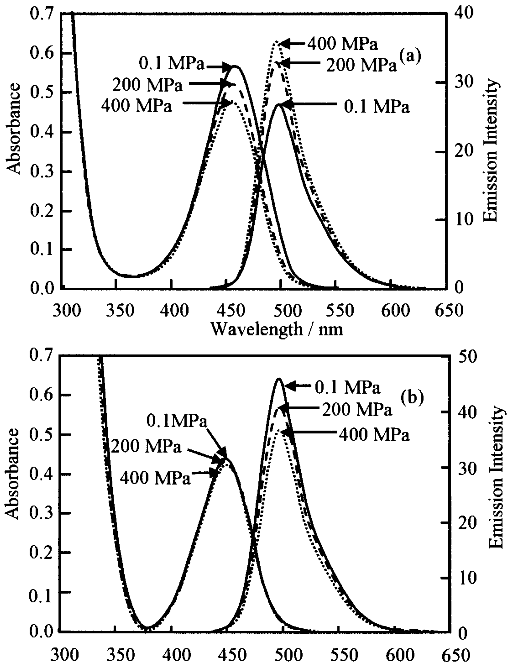

Figure 2. Absorption and emission spectra of C343 with TiO_2 nanocrystallites under various pressure in MeOH (a) and in DMF (b).

TiO_2 nanocrystallites were prepared by hydrolysis of $TiCl_4$ as previously reported.[8] Average diameter of TiO_2 prepared in this way was reported to be 2–4 nm. The aqueous solution (2 mL, 500 mM) was evaporated under reduced pressure and dissolved into 2 mL of MeOH or DMF. A colorless transparent dispersion was obtained. The UV-Vis absorption spectra and fluorescence spectra under the high pressure condition were simultaneously measured with high-pressure optical cells shown in Figure 1 (PCI-400: TERAMECS, Japan). A hand pump (TP-500: TERAMECS, Japan) was employed to compress samples up to 400 MPa. For the measurements, 4 ml of MeOH or DMF solution containing C343 (10 μM) and TiO_2 nanocrystallites (1.0 mM) was used.

Figure 2 shows absorption and emission spectra of C343 with TiO_2 nanocrystallites in MeOH (a) and in DMF (b) under various pressures. The quantum yield of the emission was estimated from the peak area of the emission spectrum and absorption intensity at 450 nm.[9] Figure 3 shows the pressure dependence of the quantum yield. Under ambient pressure, the yield in MeOH was smaller than that in DMF. In MeOH, the emission efficiency increased to 0.22 from 0.14 as pressure increased to 400 MPa. On the other hand, the efficiency in DMF decreased to 0.25 at 400 MPa from 0.33 at 0.1 MPa.

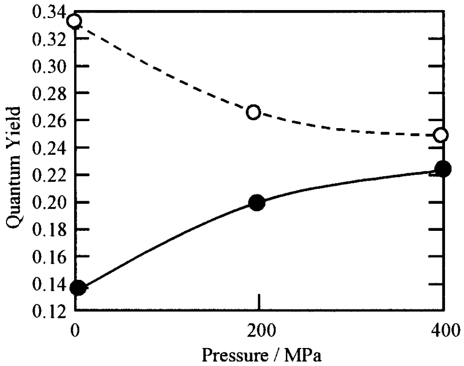

Figure 3. Pressure effect on quantum yield of the emission of C343 with TiO_2 nanocrystallites in MeOH (closed circle) and in DMF(open circle).

To estimate adsorption strength of the dye on TiO_2 surface, we measured the adsorption isotherm of C343 onto TiO_2 powder (P-25: Degussa) under the high pressure condition.[11] A MeOH or DMF solution containing TiO_2 (ca. 10 mg) and C343 (20 μM to 100 μM) was introduced into a flexible sample bag and was placed into a high-pressure vessel (TERAMECS PV400). The sample cell was compressed to 400 MPa for 300 min to achieve the adsorption equilibrium. The amount of adsorbed dye was calculated from changes in absorbance of C343 solution after removing TiO_2 particles. Adsorption parameters were summarized in Table 1.[12] These results clearly indicate that high pressure decreases the equilibrium constant and saturated amount of adsorbed dye molecules on TiO_2 nanocrystallites for both systems of MeOH and DMF. With these results, we conclude that applying high pressure induces desorption of adsorbed dye molecules on TiO_2 nanocrystallites surface.

Table 1. Adsorption parameters of C343 onto TiO_2 (P25)

Solvent	MeOH		DMF	
Pressure (MPa)	0.1	400	0.1	400
V (mmol / g TiO_2)[a]	14.45	11.48	15.67	14.97
K[b]	191.91	52.00	86.41	47.08

[a]V is saturated amount of adsorption.
[b]K is equilibrium constant of adsorption.

Observed decrease in quenching efficiency in MeOH is explained by the increase of free dye molecules by desorption. The quenching efficiency in DMF increased in spite of the dye molecule desorbed as well as in MeOH. The quantum yields of the free dye molecule in DMF were 0.52 and 0.51 at 0.1 MPa and 400 MPa, respectively. No change in the yield was observed at high pressure. These results indicate that applying high pressure in DMF intrinsically enhances the electron transfer efficiency. Generally, the electron transfer in aprotic solvent is less efficient than that in protic solvent.[13] The efficiency improved, and became comparable to that in protic solvent, in spite of aprotic character of DMF.

Under the high pressure condition, DMF molecules may form well-aligned ordered packing structure on the surface of TiO_2 nanocrystallites nanocrystallites, because of their relatively large compressibility.[14] Such oriented molecule surrounding adsorbed dye-molecules on the surface may induce lower dielectric constant of electrochemical double layer and cause to efficient electron transfer from the dye to TiO_2 nanocrystallites with lowering the dielectric constant.[15]

The high pressure technique can be applied to control photo induced electron transfer systems. Further investigation is now in progress.

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References and Notes

\# Present address: PRESTO, Japan Science and Technology Corporation; Department of Chemistry, Graduate School of Engineering Science, Osaka University.

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9 The emission spectrum in the energy unit was divided by the intensity of absorption spectrum at the excited wavelength of 450 nm to obtain the emission efficiency. Quantum efficiencies were estimated as the emission efficiency normalized using the quantum efficiency of emission measured for free dye in MeOH under ambient pressure (0.63).[10]

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11 In the measurement of adsorption isotherm, the TiO_2 nanocrystallites could not be used because the particle size is too small to be removed by filtration. The size of employed P25 is known as 21 nm.

12 Adsorption equilibrium constant, K, and saturated amount of adsorption, a, are given by following equation. $1 / v = 1 / aKc + 1 / a$, where v and c are the adsorbed amount of adsorption and the equilibrated concentration, respectively.

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