CHEMISTRY LETTERS, pp. 2025-2028, 1993.

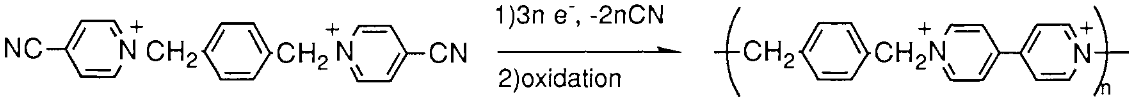
Preparation of Polyviologen-modified TiO_2 by Photocatalytic Polymerization of Bis(4-cyano-1-pyridinio)-*p*-xylene Dibromide

Tetsuyuki SAIKA,* Tomokazu IYODA,† and Takeo SHIMIDZU†
PREST, JRDC, Daiso Co. Ltd., 9 Otakasu, Amagasaki 660
†Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

Methylviologen was prepared from 4-cyano-1-methylpyridinium chroride by photocatalytic reduction using TiO_2 powder. In the similar manner, insoluble polyviologen was deposited on TiO_2 powder by photocatalytic polymerization of bis(4-cyano-1-pyridinio)-*p*-xylene dibromide. Moreover, polyviologen-polyanion complex modified TiO_2 was prepared in the presence of polyanion salt.

Recently, systems combined viologen with semiconductor have been interested in. For example, viologen has been used as an effective electron mediator in photocatalytic systems, because its low redox potential is suitable for the photoproduction of hydrogen by the reduction of protons with colloidal Pt.1-5) There have been numerous investigations on photocatalytic systems with viologen and polyviologen.6-9) In addition, polyviologen-semiconductor composites have been investigated as electrochromic and photochromic materials.10,11)

We wish to report herein on preparation of polyviologen-modified TiO_2 by photocatalytic polymerization of bis(4-cyano-1-pyridinio)-*p*-xylene dibromide (BCPPX). Recently, we reported that water insoluble polyviologen films on electrodes were prepared by cathodic electrolyses of bis(4-cyano-1-pyridinio) derivatives under weak basic conditions.12) Bis(4-cyano-1-pyridinio) derivatives were reduced to 4-cyano-1,4-dihydro-4-pyridyl radicals (abbreviated 4-cyano-4-pyridyl radical hereafter), which were coupled successively to form polyviologen films with elimination of cyanide ions, at -0.64 – -0.74 V vs. SCE. The polyviologen films deposited by this electropolymerization were insoluble in water or common organic solvents caused by spontaneous cross linkings.

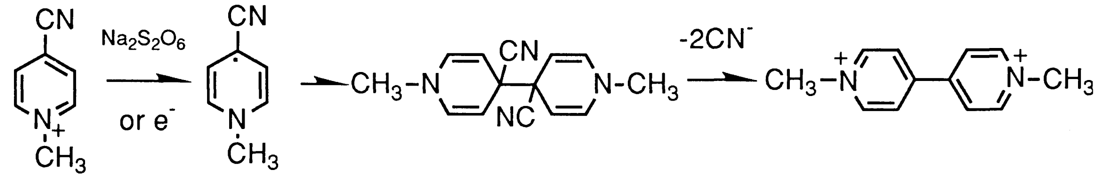


The photocatalytic reaction on illuminated titanium oxide surfaces has included reduction with conduction band electrons and oxidation with valence band holes. The conduction band potential of TiO_2 is calculated from the equation following:

$$E_{CB} = -0.11 - 0.059\text{pH} \quad \text{V} \quad (vs.\ \text{NHE})$$

using pH.13) Under basic conditions more than pH 7, the conduction band potential is enough to reduce the 4-cyano-1-pyridinio derivatives to the 4-cyano-4-pyridyl radical which forms a viologen skeleton.

There have been some reports that viologen cation radicals has been observed in spectroscopic measurements of a chemical[14,15] or electrochemical[16-18] reduction of a 4-cyano-1-methylpyridinium salt. The reduced 4-cyano-1-methyl-4-pyridyl radicals coupled to form a viologen skeleton with the elimination of two cyanides.



In order to confirm that a photocatalytic system can reduce 4-cyano-1-pyridinio derivatives to form viologen, we have investigated the photocatalytic reduction with 4-cyano-1-methylpyridinium chloride (CMP).[19] TiO_2 powder (anatase form, Titan Kogyo STT-65C) was suspended in a solution of CMP (0.01 mol dm^{-3}) containing 5%-ethanol as a sacrificial reductant, conditioned at pH 8 by sodium hydrogencarbonate. During irradiation at 360 nm (500 W Xenon lamp associated with a 360 nm broad band filter, Toshiba UV-D36A), the suspension turned blue-violet, which was indicative of the viologen cation radical. Figure 1 shows the NMR spectrum change during the reaction. Before irradiation, AB-doublet signals at 8.51 (α-protons) and 9.11 (β-protons) and a methyl-proton signal at 4.73 were assigned to CMP. After UV irradiation for 3 days, new AB-doublet signals at 8.22 (α-protons) and 8.82 (β-protons) ppm and a methyl-proton signal at 4.1 ppm appeared and were assigned to methylviologen. Moreover, methylviologen was isolated from the reaction solution by column chromatography on Sephadex® LH-20 and all spectrum data agreed with the authentic sample.

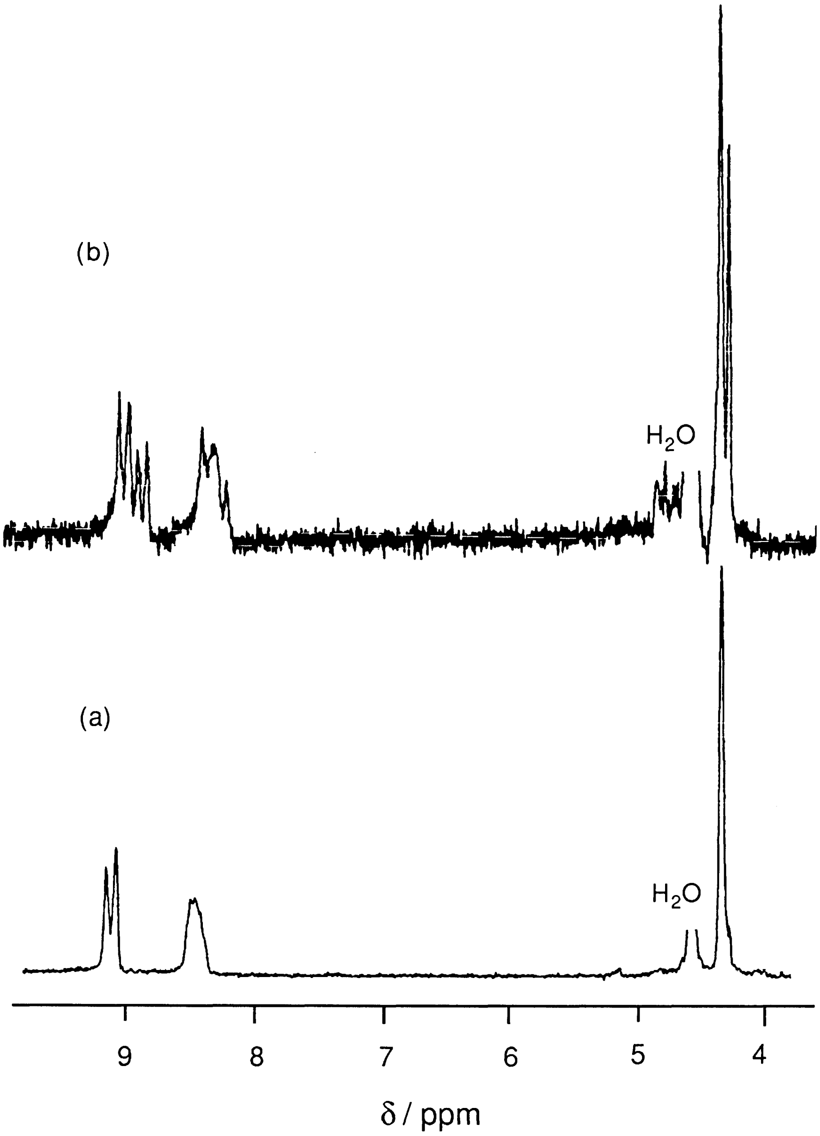


Fig. 1. ^{1}H NMR changes of CMP befor irradiation (a) and after (b).

BCPPX,[20)] having reduction potential at -0.64 V *vs.* SCE, was polymerized by cathodic electrolysis and then the insoluble polyviologen which resulted was deposited onto an electrode.[11)] BCPPX (0.01 mol dm^{-3}) was also polymerized by photocatalytic reduction with the above system, which was a suspension of TiO_2 powder containing 5%-ethanol at pH 8. During irradiation at 360 nm, the suspension turned blue-violet, which was indicative of the viologen cation radical. After irradiation for 6 h, the TiO_2 powder was collected and washed with water by centrifugation. Elemental analysis of the powder showed 7.89% organic component. The 5.2% nitrogen, which was a half volume of BCPPX (N, 11.83%) suggested the elimination of two cyanide ions.[21)] When the washed powder, transferred to clean 5%-ethanol, was irradiated at 360 nm, it turned blue-violet, and its absorption spectrum (Fig. 2(a))[22)] was assigned to the viologen cation radical dimer with an absorption maximum at 550 nm, similar to the electropolymerized film.[12)] This showed the polyviologen-modified TiO_2 was prepared by the photocatalytic polymerization of BCPPX in a manner similar to the electropolymerization. The cation radical state of polyviologen-modified TiO_2 was oxidized to the dication state by air. This photocatalytic reduction and the oxidation by air recurred several times.

Moreover, polyviologen-polyanion complex-modified TiO_2 was prepared in a similar way to the polyviologen-modified TiO_2. We reported a polyviologen-polyanion complex film was prepared by electropolymerization of BCPPX in a solution containing potassium polyethylenesulfonate (PESK) as a supporting electrolyte.[12)] In the electropolymerization, the modification rate of polyviologen with PESK was four times higher than that with monomeric anions as supporting electrolytes, because the polymerized viologen formed a water-insoluble complex with polyethylenesulfonate ions *in situ.*

BCPPX (0.01 mol dm^{-3}) was polymerized by photocatalytic reduction of TiO_2 in a suspension containing 0.1 mol dm^{-3} PESK and 5%-ethanol at pH 8 with UV irradiation for 2 h. Poly-viologen-polyethylenesulfonate (PES) modified TiO_2 showed photo-responsibility similar to that of poly-viologen-modified TiO_2 (Fig. 2(b)).[22)]

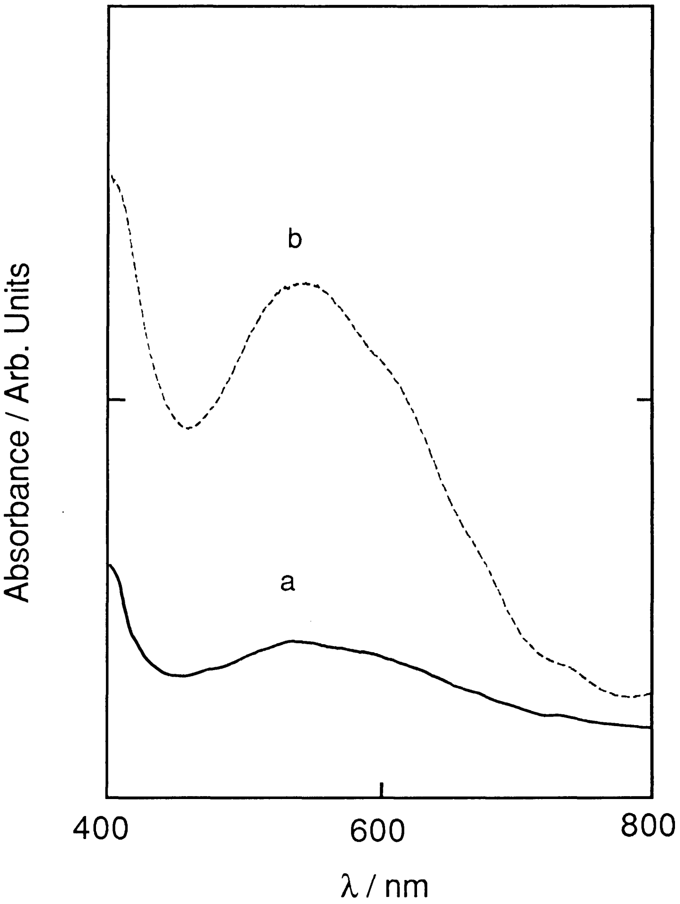


Fig. 2. Absorption spectra of the polyviologen-modified TiO_2 (a) and the polyviologen-PES-modified TiO_2 (b).

These shows basic strategy to prepare polyviologen-semiconductor composites. The polyviologen-modified TiO_2 and the polyviologen-PES-modified TiO_2 showed light responsibility as viologen dications to the blue-violet cation radical caused by photocatalytic reduction of TiO_2 with alcohol as a sacrificial reductant. Since viologen is a good electron mediator in the photocatalytic system, polyviologen-modified TiO_2 is expected to work as a unique photocatalyst. With the light responsibility, these modified TiO_2 will use light writing memory or display.

References

1) D. Duonghong, E. Borgarello, and M. Grätzel, *J. Am. Chem. Soc.*, **103**, 4685 (1981).
2) D. S. Miller, A. J. Bard, G. McLendon, and J. Ferguson, *J. Am. Chem. Soc.*, **103**, 5336 (1981).
3) E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca, and M. Grätzel, *J. Am. Chem. Soc.*, **103**, 6324 (1981).
4) T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Comm.*, **1980**, 694.
5) P.-A. Brugger, P. Cuendet, and M. Grätzel, *J. Am. Chem. Soc.*, **103**, 2923 (1981).
6) T. Nakahira and M. Grätzel, *J. Phys. Chem.,* **88**, 4006 (1984).
7) R. E. Sassoon, S. Gershuni, and J. Rabani, *J. Phys. Chem.*, **89**, 1937 (1985).
8) Y. Nosaka and M. A. Fox, *Langmuir*, **3**, 1147 (1987).
9) K. Ageishi, T. Endo, and M. Okawara, *J. Polym. Sci., Polym. Chem.*, **19**, 1085 (1981).
10) B. Ohtani, T. Atsumi, S. Nishimoto, and T. Kagiya, *Chem. Lett.*, **1988**, 295.
11) K. Nomura, K. Hirayama, T. Ohsaka, M. Nakanishi, O. Hatozaki, and N. Oyama, *J. Macromol. Sci.-Chem.*, **A26**, 593 (1989).
12) T. Saika, T. Iyoda, and T. Shimidzu, *Bull. Chem. Soc. Jpn.*, **66**, 2054 (1993).
13) D. Duonghong, J. Ramsden, and M. Grätzel, *J. Am. Chem. Soc.*, **104**, 2977 (1982).
14) W. M. Schwarz, E. M. Kosower, and I. Shain, *J. Am. Chem. Soc.*, **83**, 3164 (1961).
15) E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, **86**, 5524 (1964).
16) I. Carelli and M. E. Cardinali, *J. Electroanal, Chem.*, **124**, 147 (1981).
17) A. Webber, E. K. Eisner, J Osteryoung, and J. Hermolin, *J. Electrochem. Soc.*, **129**, 2725 (1982).
18) A. Webber and J. Osteryoung, *J. Electrochem. Soc.*, **129**, 2731 (1982).
19) F. H. Quina, M. J. Politi, I, M, Cuccovia, E. Baumgarten, S. M. Martins-Franchetti, and H. Chaimovich, *J. Phys. Chem.,* **84**, 361 (1980).
20) BCPPX was prepared according to Ref.12. Anal. Found: C, 50.51; H, 3.40; Br, 33.58; N, 11.83%. Calcd for $C_{20}H_{16}Br_2N_4$: C, 50.87; H, 3.42; Br, 33.84; N, 11.87%.
21) Anal. Found: C, 45.2; H, 5.8; N, 5.2% (recalculated as a 100% organic component), Calcd for Poly[(xylene-a,a'-dyl-substituted viologen], $C_{18}H_{16}Br_2N_2$: C, 51.5; H, 3.84, N, 6.67%.
22) Absorption spectrum was measured with reflectance spectrophotometry. After a suspension of modified TiO_2 was irradiated for 30 min, the TiO_2 was precipitated in a quartz cell. It was measured through the cell bottom using an optical fiber system (Otsuka Electronics MCPD-1000).

(Received August 19, 1993)