Photocatalytic Electron Transfer in Hybrid Titania Nanosheets Studied by Nanosecond Laser Flash Photolysis

Takashi Tachikawa, Tatsuto Yui,[†] Mamoru Fujitsuka, Katsuhiko Takagi,[†] and Tetsuro Majima*
The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047
[†]*Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603*

(Received August 29, 2005; CL-051104)

The electron-transfer reaction in the composite films of a *meso*-(tetramethylpyridinium)porphyrin (TMPyP)–mesoporous silica (MPS) (TMPyP–MPS) and a methyl viologen (MV^{2+})–titania nanosheet (TN) (MV^{2+}–TN) was studied by nanosecond transient absorption measurements. The effects of the (TMPyP–MPS) layer on the one-electron reduction process of MV^{2+} were examined.

Metal oxide semiconductor films are under intensive investigation for a variety of optoelectronic applications such as dye-sensitized solar cells, intercalation batteries, and electrochromic and electroluminescent displays, as well as environmental sensors and biosensors.[1–4] In particular, the laminated hybridization of organic dyes and electron acceptors spatially separated by mesoporous silica (MPS) and inorganic layered materials has attracted much attention in recent years for its role in the suppression of the back electron transfer between the one-electron-reduced and the one-electron-oxidized species in visible light responsive photocatalytic systems.[5–8] Recently, Takagi and coworkers fabricated a hybrid film consisted of a titania nanosheet (TN) including an electron acceptor (methyl viologen, MV^{2+}) and a cubic MPS including an organic dye (*meso*-(tetramethylpyridinium)porphyrin, TMPyP) and the resulting tetrad hybrid film ((TMPyP–MPS)/(MV^{2+}–TN)) (Figure 1) was confirmed to exhibit photofunctionality for UV-light-induced charge separations.[8] However, it is still unclear how such excitations induce charge separation within the tetrad hybrid films to generate the observed photocatalytic activity, becase of the fast interfacial electron-transfer processes.

In the present study, we have investigated the one-electron reduction reaction of MV^{2+} independently included within TN during the photocatalytic reactions using the nanosecond transient absorption spectroscopy. As is well known, the transient absorption technique is a powerful tool for the investigations of mechanisms involving photochemical reactions. The effects of the TMPyP–MPS layer on the one-electron reduction process of MV^{2+} were discussed.

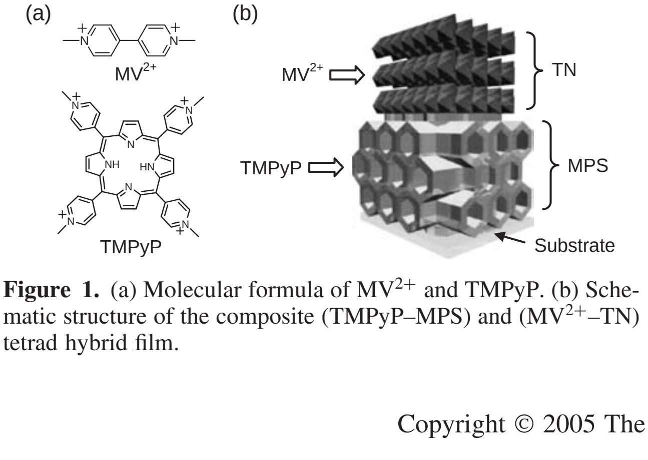

Figure 1. (a) Molecular formula of MV^{2+} and TMPyP. (b) Schematic structure of the composite (TMPyP–MPS) and (MV^{2+}–TN) tetrad hybrid film.

The laminated hybrid composite consecutively stacked with (TMPyP–MPS) and (MV^{2+}–TN) was synthesized by the reported procedures.[8] In a typical method, an aqueous MPS precursor gel suspension of cetyltrimethylammonium chloride was spin-coated on a quartz glass and then calcinated at 500 °C for 3 h. The thin films were soaked for 1.0 h in an aqueous solution of TMPyP at ambient temperature, leading to the formation of brownish colored films. The absorption spectra of the films showed a sharp Soret band at 430 nm, which is 5-nm red-shifted when compared with the band in aqueous solution. This spectral shift suggests the nonaggregated adsorption of TMPyP in the mesopores of the MPS. The (TMPyP–MPS) composite films were hybridized with TN nanosheets by electrophoretic or casting deposition and were then soaked in an aqueous solution of MV^{2+} for 4 h at ambient temperature. The TMPyP and MV^{2+} molecules are spatially separated by the intervention of MPS and TN.

Time-resolved absorption measurements were performed using the third harmonic generation (355 nm, 5 ns FWHM) from a Q-switched Nd:YAG laser (Continuum, Surelite II-10) for the excitation operated with a temporal control by a delay generator (Stanford Research Systems, DG535). The analyzing light from a pulsed 450 W Xe-arc lamp (Ushio, UXL-451-0) was collected by a focusing lens and directed through a grating monochromator (Nikon, G250) to a silicon avalanche photodiode detector (Hamamatsu Photonics, S5343). The transient signals were recorded with a digitizer (Tektronix, TDS 580D). All measurements were carried out at room temperature.

Figure 2 shows the transient absorption spectra observed during the 355-nm laser flash photolysis of the (TMPyP–MPS)/(MV^{2+}–TN) composite film. The broad transient absorption bands with two maxima around 470 and 600 nm appeared after the laser flash. The absorption band at 500–700 nm is attributable to $MV^{\bullet+}$.[9] A similar absorption band due to $MV^{\bullet+}$ was also observed for the (MV^{2+}–TN) film. The absence of the expected rise shows that the electron transfer from an electron in the conduction band of TN (e_{CB}^{-}) to MV^{2+} was completed within the laser duration of 5 ns. On the other hand, the transient absorption band at 450–500 nm and the absorption bleaching at <450 and 520 nm are attributable to TMPyP in the triplet excited state ($^{3}TMPyP^{*}$) ($\varepsilon_T = 28600\,M^{-1}\,cm^{-1}$ at 450 nm, $\Phi_T = 0.92$),[10] which is generated by the direct excitation of TMPyP included within MPS, and the depletion of TMPyP, respectively. It should be noted that the lifetimes (>3 ms) of both $MV^{\bullet+}$ and $^{3}TMPyP^{*}$ are quite longer than those (<10 μs) in air-saturated water.[9,10] To examine the effect of the (TMPyP–MPS) layer on the one-electron reduction process of MV^{2+}, the obtained ΔO.D. values at

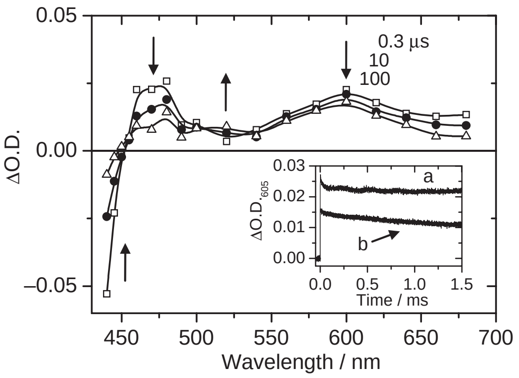

Figure 2. Transient absorption spectra observed at 0.3, 10, and 100 μs during the 355-nm laser flash photolysis of the (TMPyP–MPS)/(MV^{2+}–TN) composite film. Inset: time traces observed at 605 nm for the (TMPyP–MPS)/(MV^{2+}–TN) (a) and (MV^{2+}–TN) (b) films.

605 nm (ΔO.D.$_{605}$) were tentatively compared. As shown in Figure 3, the relatively high ΔO.D.$_{605}$ value (0.024 ± 0.002) was observed at 50 μs after the laser pulse for the (TMPyP–MPS)/(MV^{2+}–TN) composite film, compared with that (0.016 ± 0.003) for the MV^{2+}–TN film.[11] Considering the fact that ^{3}TMPyP* has some absorption at 605 nm (ΔO.D.$_{605} \approx 0.003$ for the (TMPyP–MPS)/(MV^{2+}–TN) film), the net $\Delta\Delta$O.D.$_{605}$ value is estimated to be 0.005–0.006, which corresponds to increase by about 30%.

Previously, Takagi and co-workers reported that the (TMPyP–MPS)/(MV^{2+}–TN) composite film was irradiated for 60 min by visible light of 390–550 nm which was absorbed only by the TMPyP; however, no detectable spectral changes in the absorption was observed.[8] This could be explained by the fact that TN has a more negative conduction band potential at -1.02 V vs SCE[12] than the redox potential of TMPyP in the singlet excited state ($E^{\circ}(\mathrm{TMPyP}^{\bullet+}/^{1}\mathrm{TMPyP}^{*}) = -0.73$ V vs SCE).[13] In contrast, UV light irradiation at 270–380 nm turned the color of the hybrid films from brown to blue, which is due to the reduction of MV^{2+}. Under these conditions, TN could be seen to act as a photocatalyst to produce a charge-separated state. They have also observed the decomposition of the TMPyP accommodated in the MPS with the reduction of MV^{2+} incorporated in the TN interlayers, and concluded that the photochemically formed holes were able to migrate to the TMPyP through the cubic MPS nanocavities.[8]

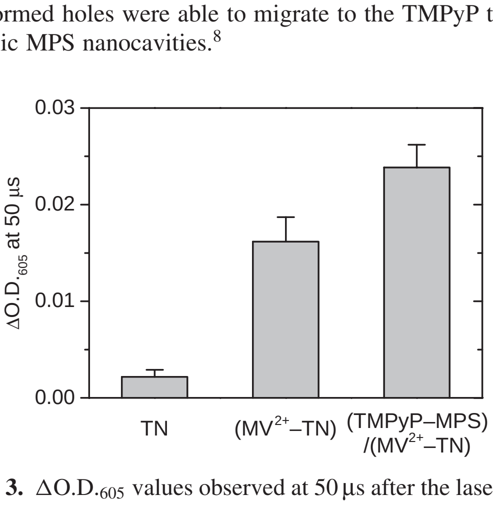

Figure 3. ΔO.D.$_{605}$ values observed at 50 μs after the laser pulse.

Thus, the proposed reaction mechanisms can be expressed by the equations,

$$\mathrm{TN} + h\nu \rightarrow \mathrm{e_{CB}}^{-} + \mathrm{h_{VB}}^{+}, \qquad (1)$$

$$\mathrm{e_{CB}}^{-} + \mathrm{MV}^{2+} \rightarrow \mathrm{MV}^{\bullet+}, \qquad (2)$$

$$\mathrm{h_{VB}}^{+} + \mathrm{TMPyP} \rightarrow [\mathrm{TMPyP}]_{\mathrm{ox}}, \qquad (3)$$

where $\mathrm{h_{VB}}^{+}$ is the hole in the valence band of TN and $[\mathrm{TMPyP}]_{\mathrm{ox}}$ is the oxidized TMPyP. Unfortunately, although the no direct evidence for the electron-transfer reaction from TMPyP to $\mathrm{h_{VB}}^{+}$ was obtained, the observed increase in ΔO.D.$_{605}$ suggests that the (TMPyP–MPS) layer could assist the charge-separation processes at the interface between TN and MPS during the photocatalytic reactions. As shown in the inset of Figure 2, the slow decay process observed for the (TMPyP–MPS)/(MV^{2+}–TN) composite film (a), compared with that for the (MV^{2+}–TN) film (b), also supports the fact that the recombination processes between $\mathrm{MV}^{\bullet+}$ and $\mathrm{h_{VB}}^{+}$ are inhibited by the scavenging of $\mathrm{h_{VB}}^{+}$ by TMPyP at the interface between TN and MPS.

In summary, we observed the one-electron reduction reaction of MV^{2+} during the 355-nm laser flash photolysis of the (TMPyP–MPS)/(MV^{2+}–TN) composite film. The photocatalytic one-electron reduction process of MV^{2+} was enhanced by lamination with the (TMPyP–MPS) layer. It is anticipated that these novel hybrid materials will have potential applications in electrode materials, catalysis, and other fields.

We are grateful to Ms. Takako Tsuchino for preparation of the TNs. This work has been partly supported by a Grant-in-Aid for Scientific Research (Project No. 17105005, Priority Area (417), 21st Century COE Research, and others) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japanese Government.

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Published on the web (Advance View) October 8, 2005; DOI 10.1246/cl.2005.1522