Visible-light-induced electron transfer in intercalation-type composites organized on photocatalytically active layered niobate

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We prepared multicomponent composites of layered hexaniobate, a photocatalytically active layered semiconductor, with cationic organic species of methylviologen as an electron acceptor, proflavine as a photosensitizing dye, and triethanolammonium as a sacrificial donor. Two types of composites with different location of methylviologen, which was incorporated in the interlayer spaces or adsorbed on the external surfaces, were obtained. Visible light irradiation caused photo reduction of methylviologen in the composites, which was ascribed to the photoinduced electron transfer initiated by the photoexcitation of the proflavine dye. The location of methylviologen affected aggregation of the photoreduced methylviologen. A mixture of the three organic species without the niobate did not cause the reduction of viologen but self-decomposition of the proflavine dye under the same irradiation conditions, which indicated that the semiconducting niobate layers were indispensable for transferring electrons from the photoexcited dye to the acceptor.

Key-words : Layered niobate, Intercalation, Photoinduced electron transfer, Methylviologen, Acridine dye

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1. Introduction

Layered niobates and titanates, wide band-gap semiconducting and ion-exchangeable oxides possessing both photocatalytic activities\(^{13-16}\) and intercalating properties,\(^{1,5}\) are promising materials for novel photocatalytic systems. Intercalation compounds of these oxides can show electronic/energetic interactions between the photocatalytically active layers and the guest molecules to realize unusual photochemical behaviors.\(^{1,5}\) A typical example is seen for the combination of these oxides with methylviologen dication (MV\(^{2+}\)) that has been utilized as an electron relay in photosynthesis conversion systems because of its characteristic redox behavior.\(^{2,9}\) When MV\(^{2+}\) cations are intercalated in the interlayer spaces of the layered niobates and titanates, electron transfer from the photocatalytically active semiconducting oxide layers to the incorporated MV\(^{2+}\) cations occurs to yield methylviologen radical cations (MV\(^{1+}\)) upon UV irradiation.\(^{10,12}\) In addition, our recent study has demonstrated that the photoinduced electron transfer also occurs even when the MV\(^{2+}\) cations are not intercalated in the interlayer spaces but adsorbed on the external surfaces.\(^{13}\) The MV\(^{2+}\) cations are converted to the MV\(^{1+}\) monomers when they are intercalated, while the MV\(^{1+}\) dimers form on the external surfaces based on different mobility of the acceptor molecules. In these systems, the photochemical communications between the oxide layers and intercalated/adsorbed molecules are driven by excitation of the semiconductor layers with UV light because the band gap of the layered niobates and titanates is rather wide (>3.4 eV).\(^{11}\)

Another type of photochemical events has been reported for intercalation compounds of the layered niobates and titanates with dyes, where the photocatalyses can be initiated by photoexcitation of the intercalated dye molecules with visible light. Photoinduced electron/energy transfer from the intercalated dye species to the oxide layers has been achieved in the intercalation compounds or structurally compatible layer-by-layer assemblies of the semiconducting oxides with a ruthenium complex,\(^{14-16}\) porphyrin,\(^{17,18}\) cyanine\(^{19}\) and rhodamine dyes,\(^{20}\) and polyaniline.\(^{21}\) These studies provide important basis of photosensitizing the semiconducting layers required for effective utilization of solar energy, and thus, one can construct multicomponent systems for visible-light-induced electron transfer, which is a key process of artificial photosynthesis, by combining an electron acceptor and photosensitizer with the layered niobates and titanates. In fact, a layered assembly of a titanoniobate incorporating MV\(^{2+}\) and porphyrin cations has been prepared by sequential casting of two intercalation compounds of the layered titanoniobate with MV\(^{2+}\) and porphyrin on a substrate.\(^{22,23}\) This assembly shows visible-light-induced electron transfer from the porphyrin molecules to the MV\(^{2+}\) cations. However, the porphyrin molecules that are photoexcited to transfer the electrons to the MV\(^{2+}\) cations passing through the oxide layers are irreversibly decomposed in this system. In addition, since there are many possible photosensitizers other than porphyrins, various other photocatalytic systems that respond to visible light can be constructed.

In the present study, we have prepared multicomponent composites that show visible-light-induced electron transfer on layered hexaniobate K\(_2\)Nb\(_6\)O\(_{17}\) possessing photocatalytic activity. Cationic proflavine (PF\(^{2+}\), an acridine dye), MV\(^{2+}\), and triethanolammonium cation (TEAH\(^{+}\)) have been used as a photosensitizer, electron acceptor, and sacrificial donor, respectively; the last species has been added in order to avoid irreversible decomposition of the dye observed in the previous system.\(^{22,23}\) There are a few reports on photosensitization of
semiconductor photocatalysts by acridine dyes. We have adopted a facile preparation method by which only MV$^{2+}$ and TEAH$^+$ cations are intercalated but the other species are introduced onto the external surfaces with a simple soaking technique, because our previous study indicates that photofunctional molecules located on the external surfaces of the niobate can contribute to the photochemical reactions as well as those intercalated.

2. Experimental section

We prepared two samples composed of K$_3$Nb$_5$O$_{17}$, MV$^{2+}$, TEAH$^+$ and PF$^+$ species. For the first sample, powdery K$_3$Nb$_5$O$_{17}$·3H$_2$O, which was prepared with the method reported previously, was at first allowed to react with an excess amount of an aqueous solution of MV$^{2+}$ chloride at 333 K for 2 weeks to intercalate the MV$^{2+}$ ions. After thorough washing and drying, the product, which is called Nb$_5$O$_{17}$-MV hereafter, was dispersed in a binary aqueous solution of TEAH$^+$ chloride and PF$^+$ hemisulfate for overnight, and then the suspension was drop cast on a Pyrex plate. The film sample obtained by this procedure is named (Nb$_5$O$_{17}$-MV)/TEAH/PF. Preparation of the second sample was started by the reaction of K$_3$Nb$_5$O$_{17}$·3H$_2$O with an excess amount of an aqueous TEAH$^+$ solution at 333 K for 2 weeks. The product, an intercalation compound of the niobate and TEAH$^+$ called as Nb$_5$O$_{17}$-TEAH hereafter, was dispersed in a binary aqueous solution of MV$^{2+}$ and PF$^+$ for overnight, and then a drop cast film of the suspension was obtained. The film sample prepared by this sequence is designated as (Nb$_5$O$_{17}$-TEAH)/MV/PF. A control sample that excluded the niobate component was prepared by drop-casting a ternary aqueous solution of MV$^{2+}$, TEAH$^+$, and PF$^+$ species; it is named MV/TEAH/PF.

Photochemical behavior of the composites was examined by irradiating a film sample cast on Pyrex plate with visible light (≥440 nm) using a 500-W Xe lamp equipped with a cutoff and heat-absorbing filters under a nitrogen atmosphere. Response to the visible-light irradiation was monitored with visible absorption spectra of the films using a transmission mode. Structure of the samples was characterized with XRD.

3. Results and discussion

The layered niobiate K$_3$Nb$_5$O$_{17}$ is intercalated with the organic species contacted with the niobate at first among the three organic cations (MV$^{2+}$, TEAH$^+$, and PF$^+$) to form intercalation-type multicomponent composite films. Figure 1 shows the XRD patterns of samples. The diffractions of Nb$_5$O$_{17}$-MV yielded by the reaction of K$_3$Nb$_5$O$_{17}$ with MV$^{2+}$ [Fig. 1(b)] shows the intercalation of MV$^{2+}$ ions as indicated by the increase in the basal spacing from 1.88 nm (K$_3$Nb$_5$O$_{17}$·3H$_2$O) to 2.2 nm (intercalation compound). The XRD pattern of the final product (Nb$_5$O$_{17}$-MV)/TEAH/PF with the basal spacing of 2.3 nm is similar to that of Nb$_5$O$_{17}$-MV although broadening of the diffraction peaks is observed; additional interlayer expansion by the reaction with TEAH$^+$ and PF$^+$ is very small. On the other hand, the diffraction pattern of Na$_3$O$_{17}$-TEAH with the basal spacing of 2.4 nm indicates the intercalation of TEAH$^+$ ions, and the final product of (Na$_3$O$_{17}$-TEAH)/MV/PF shows the diffactogram resembling that of Na$_3$O$_{17}$-TEAH with a similar basal spacing of 2.3 nm.

These results strongly suggest that both of the final products, (Na$_3$O$_{17}$-MV)/TEAH/PF and (Na$_3$O$_{17}$-TEAH)/MV/PF, basically retain the interlayer structures of the preformed intercalation compounds, Nb$_5$O$_{17}$-MV and Nb$_5$O$_{17}$-TEAH for (Nb$_5$O$_{17}$-MV)/TEAH/PF and (Na$_3$O$_{17}$-TEAH)/MV/PF, respectively. In other words, cointercalation of MV$^{2+}$, TEAH$^+$, and PF$^+$ ions is hardly attained. This is rational because the reaction conditions of the preformed intercalation compounds with the additional species (soaking at room temperature for overnight) are much moderate that those of the intercalation (333 K for 2 weeks). Figure 2 shows schematic structures of the composites. Similar negligible occurrence of the cointercalation or displacement of the preintercalated MV$^{2+}$ (or TEAH$^+$) ions for TEAH$^+$ (or MV$^{2+}$) ions in the interlayer space of the niobate with a moderate soaking procedure has been observed in our previous study.

Visible spectroscopy informs the status of PF$^+$ species in the multicomponent composites. Figures 3-5 show the spectra of the samples. They exhibit an intense absorption band due to the absorption of PF$^+$ monocations at around 460 nm. Both of the composites (Na$_3$O$_{17}$-MV)/TEAH/PF and (Na$_3$O$_{17}$-TEAH)/MV/PF including the niobate layers show the absorption maximum at 470 nm irrespective of the difference in the preparation procedure. The MV/TEAH/PF sample excluding the niobate exhibits the maximum at 450 nm. Whereas all the
samples show the band at red-shifted wavelengths compared with that of an aqueous PF\(^{+}\) solution (440 nm), the composite samples including the niobiate exhibit the absorption maximum at the largely shifted position. This result suggests strong interactions between the PF\(^{+}\) ions and the niobiate layers, the interactions which similarly occur for both of (Nb\(_6\)O\(_{17}\)−MV)/TEAH/PF and (Nb\(_6\)O\(_{17}\)−TEAH)/MV/PF, where the dye species are supposed to be present dominantly on the external surface of the niobiate.

The composite films composed of the niobiate, MV\(^{2+}\), TEAH\(^{+}\), and PF\(^{+}\) species show photochemical response upon irradiation of visible light longer than 440 nm. Figure 3 shows spectral change of the (Nb\(_6\)O\(_{17}\)−MV)/TEAH/PF sample. While whole the spectral shape is almost retained after the irradiation for 60 min, certain absorption increase is observed at the wavelengths around 400 and 600 nm. The difference spectra [Fig. 3(B)] indicate the spectral profile characteristic to the MV\(^{2+}\) cations; the MV\(^{2+}\) monomer with the absorption bands at 405 and 615 nm and the dimer with the bands at 360 and 560 nm are both generated.\(^9\) This result indicates that visible-light-induced electron transfer occurs in the composite to reduce the MV\(^{2+}\) species. The slightly negative absorbances at around 450 nm in the difference spectra indicate a little decomposition of the PF\(^{+}\) dye. The simultaneous generation of the MV\(^{2+}\) monomers and dimers is observed when the MV\(^{2+}\) cations are intercalated between the niobiate layers, as has been reported in our previous paper.\(^13\) Thus, the photochemical behavior of the viologen species is consistent with the intercalated structure suggested by the XRD analysis.

The (Nb\(_6\)O\(_{17}\)−TEAH)/MV/PF sample also shows the visible-light-induced electron transfer similar to that observed for (Nb\(_6\)O\(_{17}\)−MV)/TEAH/PF while only the MV\(^{2+}\) dimers are generated. Figure 4 shows the visible spectra of this sample before and after the irradiation, and the difference spectra exhibit characteristic profile of the MV\(^{2+}\) dimers with absorption maxima at 360 and 560 nm. In this sample, photodecomposition of the PF\(^{+}\) dye is negligible. Our previous study has revealed that diimic MV\(^{2+}\) cations are obtained when the MV\(^{2+}\) molecules located on the external surface, which provides mobile environment compared with the interlayer spaces because of weak steric restriction.\(^13\) Similar situation of the MV\(^{2+}\) molecules is supposed to be the case for the (Nb\(_6\)O\(_{17}\)−MV)/TEAH/PF composite as deduced from the XRD results.

Contribution of the niobiate layers to the visible-light-induced electron transfer in the multicomponent composites of the niobiate, MV\(^{2+}\), TEAH\(^{+}\), and PF\(^{+}\) species is confirmed by the behavior of the control sample MV/TEAH/PF that does not contain the niobiate layers. As seen in the visible spectra shown in Fig. 5, this sample does not cause reduction of MV\(^{2+}\) to MV\(^{2+}\) upon the irradiation of visible light; otherwise observed is photodecomposition of the PF\(^{+}\) dye. This result indicates that the photoenergy absorbed by the PF\(^{+}\) cations is not utilized to drive the reduction of MV\(^{2+}\) in the absence of photocatalytically active niobate layers.

From these results, we suppose that the visible-light-induced electron transfer in the multicomponent composites involves photosensitization of the niobate layers by the PF\(^{+}\) dye. The PF\(^{+}\) molecules photoexcited by the visible light transfer electrons to the niobiate layers, which have been suggested to be interacting with the dye molecules because of the hypochromic shift of the absorption band in the visible spectrum. The electrons migrate on the semiconducting oxide layers, as has been reported in previous studies,\(^20,22,28\) and meet the MV\(^{2+}\) cations to generate the MV\(^{2+}\) species. This mechanism can be rationalized by previous studies in an aqueous solution where photoexcited PF\(^{+}\) reduces MV\(^{2+}\).\(^29\) The PF\(^{+}\) cations after the electron transfer to the niobate layers would be regenerated by oxidation with the TEAH\(^{+}\) cations that are added to the system as sacrificial electron donor, as evidenced by the small or negligible loss of the dye during the photoirradiation. On the other hand, the electron transfer from the photoexcited PF\(^{+}\) species would not be facilitated in the absence of niobate layers in our solid sample. Further studies are necessary to understand the details such as exact mechanism including energy-level relationship and precise location of the reaction species.

In summary, the multicomponent composites constructed on layered hexanobiate with MV\(^{2+}\), TEAH\(^{+}\), and PF\(^{+}\) cations cause visible-light-induced electron transfer. Although the cationic species is only partly intercalated into the interlayer space of niobate, the electron transfer requires the presence of photocatalytically active niobate layers. The results indicate that multicomponent systems for visible-light-energy conversion can be organized on layered semiconductors of niobates and titanates by appropriate organization of an electron acceptor, photosensitizer (dye), and sacrificial donor, which are not necessarily intercalated but can be located on external surfaces of the layered oxides.
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