



Photoinduced electron transfer between semiconducting nanosheets and acceptor molecules in the presence of colloidal clay particles



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ABSTRACT

Binary clay colloids prepared by mixing smectite and other particles can exhibit unusual properties based on physical and chemical interactions between the colloidal particles. We prepared a binary colloidal system of layered fluoroniobate (K_2NbO_3F) and synthetic hectorite (Laponite) particles and examined photoinduced electron transfer in the colloid to which electron accepting methylviologen (MV^{2+}) was added. Exfoliation and nanosheet formation of the fluoroniobate were not evidenced, but it was transformed in water to 3D crystalline species that was easily settled down. Addition of a large amount of hectorite suppressed the settlement of the fluoroniobate particles to stabilize the colloid for a few days. When MV^{2+} ions were introduced to the binary colloid, the organic species was adsorbed on the hectorite particles and electron transfer occurred from the fluoroniobate particles to the MV^{2+} ions upon UV irradiation. Addition of propylammonium ions to the system enhanced the yield and stability of the photoproduct while an optimal amount was found. This was ascribed to the scarfing hole scavenging by the propylammonium species although the photoinduced electron transfer can occur in its absence.

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1. Introduction

Photocatalytic systems using wide band-gap semiconductors have been important research subjects for a long time (Kudo and Miseki, 2009; Ohtani, 2010; Osterloh, 2008; Teoh et al., 2012). A number of semiconductor photocatalysts have been developed after the finding of photoelectrochemical water splitting over TiO_2 (Fresno et al., 2014; Fujishima et al., 2000; Gür et al., 2014; Maeda, 2011). Among the photocatalytic semiconductors, oxide nanosheets prepared by exfoliation of layered niobates and titanates in water (Ma and Sasaki, 2010) are interesting because of their high surface areas and anisotropic morphology (Kudo and Miseki, 2009; Osterloh, 2008). In fact, these nanosheets undergo UV-light-induced photocatalytic reactions such as hydrogen evolution from water (Compton et al., 2007; Compton and Osterloh, 2009; Ebina et al., 2002; Maeda et al., 2014; Okamoto et al., 2011; Sarahan et al., 2008). The nanosheet photocatalysts of layered niobates and titanates show enhanced activities compared with their mother crystals because of their high surface areas. Compositional and textural modifications of the nanosheet photocatalysts have also been examined (Allen et al., 2010; Compton et al., 2008; Nakato et al., 2015).

However, there are relatively few studies relating to controlling the colloidal state of the photocatalytic particles although the semiconductor photocatalysis is often conducted in colloidal systems. Since the colloidal state influences diffusion of the semiconductor particles as well as

the reactant and product molecules in the photocatalytic systems, it should be an important controlling factor of the photocatalytic systems. We have paid attention to aqueous colloidal systems of niobate and titanate nanosheets, which will be called nanosheet colloids hereafter, prepared by exfoliation of layered niobates and titanates in water (Miyamoto and Nakato, 2012; Nakato and Miyamoto, 2009). Because of highly anisotropic morphology of the nanosheets characterized by about 1 nm thickness and large lateral length up to several micrometers, the nanosheet colloids can provide specific environments for the semiconducting particles and coexisting molecules. We have investigated colloidal properties of these nanosheets, and clarified liquid crystallinity of the colloids (Miyamoto and Nakato, 2002, 2004; Nakato and Miyamoto, 2002; Nakato et al., 2004, 2006). The mesomorphic property of the colloids enables organization of hierarchical structures that can be controlled by external fields such as electric voltage applied to the colloids (Nakato et al., 2011, 2014a).

The niobate and titanate nanosheet colloids show unusual behavior when they are mixed with clay colloids based on phase separation. The phase separation occurs with entropic effects induced by excluded volume of the nanosheets (Bailey et al., 2015; Nakato et al., 2014b; Woolston and van Duijneveldt, 2015). When the semiconducting nanosheets prepared by exfoliation of layered hexaniobate ($K_4Nb_6O_{17}$) are mixed with the nanosheets of synthetic hectorite (Laponite) or natural montmorillonite in an aqueous medium, the binary colloids are apparently homogeneous but separated into the niobate and clay phases at a microscopic scale (Miyamoto and Nakato, 2003). This phase separation is applied to spatial separation of the electron donating semiconducting

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nanosheets and electron accepting methylviologen (MV^{2+}) molecules selectively adsorbed on the clay nanosheets (Miyamoto et al., 2007). The binary colloids undergo photoinduced electron transfer from the semiconducting niobate nanosheets to the MV^{2+} ions adsorbed on the smectite nanosheets. The charge-separated state after the electron transfer is greatly stabilized by the spatial donor–acceptor separation (Nakato et al., 2009a).

In the binary colloids of hexaniobate and smectite, the photocatalytic hexaniobate nanosheets also coexist with organic cations. The niobate nanosheets unavoidably attach propylammonium ions, which are introduced as the delamination reagent for the niobate crystals and stay as the countercations of the anionic nanosheets (Miyamoto and Nakato, 2003). The hexaniobate nanosheets lose colloidal stability with removing the propylammonium ions. However, from the photochemical point of view, the propylammonium ions can work as sacrificial electron donors to scavenge the positive holes photogenerated in the niobate nanosheets by band-gap excitation (Saraha et al., 2008). If we can prepare stable semiconductor nanosheet colloids without the aid of organic exfoliating reagents, we may control more precisely the photoprocess and obtain more information of the role of organic coexisting species in the binary colloids of the semiconductor and clay nanosheets.

Although most of the semiconducting niobates and titanates require organoammonium ions to generate their nanosheets, layered potassium fluoroniobate K_2NbO_3F has been reported to be exfoliated in water without the use of organic exfoliating reagents (Toda et al., 2002b). This material also exhibits semiconductor photocatalytic activities for dye decomposition (Yang et al., 2013). K_2NbO_3F has a layered structure consisting of fluoroniobate layers built up by corner-shared $Nb(O(F))_6$ octahedra, and the negatively charged layers are electrostatically connected via K^+ ions (Galasso and Darby, 1962; Toda et al., 2002b). The layered structure is recognized as an intergrowth of rock-salt type KF and perovskite-type $KNbO_3$ layers. Toda and coworkers have reported exfoliation of K_2NbO_3F by simply stirring in water like smectite (Toda et al., 2002b). According to their studies, the exfoliation of K_2NbO_3F yields the single-layered perovskite-type fluoroniobate nanosheets after dissolution of the rock-salt KF units, and the fluoroniobate particles can be dispersed after the removal of large particles by filtration. However, the fluoroniobate particles are thought not to be highly stable as other niobate and titanate nanosheets because the fluoroniobate particles are assembled to form $KNbO_3$ particles with a cubic perovskite structure (Sugawara et al., 2006; Toda et al., 2002a). Based on these studies, we suppose that the fluoroniobate particles can be utilized to prepare the semiconductor nanosheet colloids that do not contain organic species.

In the present study, we have examined binary colloids of a semiconducting oxide and hectorite (Laponite) particles as an extension of our previous binary system obtained from hexaniobate ($Nb_6O_{17}^-$) and hectorite nanosheets. We have used the fluoroniobate particles obtained from K_2NbO_3F as the alternative to the hexaniobate nanosheets. Although the fluoroniobate particles dispersed in water are not likely authentic nanosheets, the binary colloids with hectorite can be stabilized at high clay concentrations, and thus enable photochemical investigations and comparison with the hexaniobate system. The binary colloid to which MV^{2+} is added as the electron acceptor causes photoinduced electron transfer from the fluoroniobate particles to MV^{2+} adsorbed on the clay particles, similarly to the hexaniobate–smectite binary nanosheet colloids. Propylammonium ions, which have been used in the previous hexaniobate system as the exfoliating reagent, are introduced to the colloid independently on the fluoroniobate particles so that the effects of the coexisting organic species are demonstrated.

2. Materials and methods

2.1. Sample preparation

Potassium fluoroniobate K_2NbO_3F was prepared by the method reported by Toda and coworkers (Toda et al., 2002b). An intimate mixture

of K_2CO_3 , Nb_2O_5 , and KF with the molar ratio of 1.0:1.0:2.6 was heated at 1063 K for 1 h, and the product was ground with a mortar. XRD pattern of the product shown in Fig. 1a confirms the formation of K_2NbO_3F ; all the diffraction peaks are assigned to K_2NbO_3F . The powdery K_2NbO_3F sample was suspended in water and stirred for 24 h. The fluoroniobate dispersion was used without further treatment. Binary colloids of the fluoroniobate and hectorite particles were obtained by mixing the fluoroniobate dispersion with hectorite colloids prepared by dispersing synthetic hectorite Laponite RD (Rookwood Additives) in water. The final concentration of K_2NbO_3F was set to 1 g L^{-1} while that of hectorite was 20 g L^{-1} otherwise noted. Colloidal stability of the samples was roughly evaluated by UV–visible spectra.

2.2. Photochemical investigations

MV^{2+} dichloride salt (Tokyo Kasei Co., used as received) was added to the fluoroniobate–hectorite binary colloid with the concentration of 1.0 mmol L^{-1} , and a small portion of the sample was placed in a water-cooled ($25\text{ }^\circ\text{C}$) quartz cell (5 mm of the light-path length) capped with a rubber septum. Then, the sample was bubbled with N_2 gas for 30 min, and irradiated with UV–visible light using a 500 W Xe lamp (Ushio SX-U1500XQ) for 8 min. After the irradiation was stopped, the cell was stood with flowing N_2 in the headspace, and visible spectra of the samples were measured repeatedly. During the experiment, the cell was kept as static as possible. A hectorite-free sample was also examined for comparison.

The photochemical reaction was monitored by generation of methylviologen radical monocations (MV^{+}) after one-electron reduction of MV^{2+} based on visible spectra. The spectra were measured with a conventional transmission mode, and the amount of the MV^{+} molecules was represented by the absorption intensity determined by differential spectra obtained by subtracting the spectrum before the UV irradiation from those after the irradiation because the spectral baseline was affected by scattering of the dispersed particles. Since the fluoroniobate particles are not stably dispersed but settled in some experiments as described in Results and discussion, the spectral baseline of the sample before irradiation was corrected in such cases.

2.3. Apparatus

XRD patterns were measured by a MAC Science MX-Labo diffractometer with monochromatic $Cu\ K\alpha$ radiation. Solid component in the aqueous dispersions was measured after drop-casting the dispersion

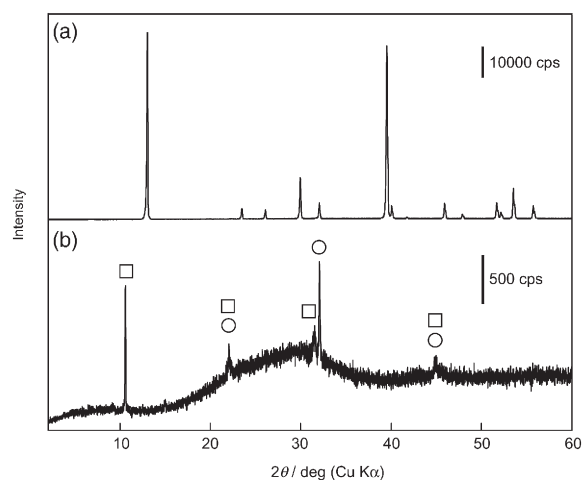


Fig. 1. XRD patterns of (a) powder K_2NbO_3F and (b) the fluoroniobate colloid (1 g L^{-1}) dried on a glass plate. Circles indicate the diffractions due to $KNbO_3$. Squares indicate the peaks assignable to $KNb_{3.76}O_6$ (Svensson, 1991) or KNb_3O_5 (Michelson et al., 1990).

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