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Photoinduced electron accumulation in colloidally dispersed wide band-gap semiconductor nanosheets

Teruyuki Nakato *, Yoshimi Yamada, Mari Nakamura, Atsushi Takahashi

Graduate School of Bio-Applications and Systems Engineering (BASE), Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan

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ABSTRACT

We investigated photoinduced electron accumulation in a colloidal system of layered hexaniobate that is known as a photocatalytically active wide band-gap semiconductor, and attempted to control the photoresponse by introducing additives into the colloid. The inorganic nanosheets were obtained by exfoliation of the layered oxide. UV-irradiation of the colloids led to electron accumulation in the nanosheets to generate reduced niobate species. Propylammonium ions introduced as the exfoliating reagent and present as the counter ions of niobate nanosheets were indicated as the electron donor that stabilized the electron-accumulating state. Yield and half-life of the reduced niobate species greatly increased by adding an appropriate amount of photochemically inert clay nanosheets, while they increased only a little by the addition of molecular electron donors such as EDTA and triethanolamine. Moreover, the molecular species diminished the enhancement effect of the clay nanosheets. The results suggested that the photochemical event was not explained by direct interactions between the semiconductor nanosheets and the additives at molecular level but governed by indirect interactions between the colloid components regulated by the colloid structure.

1. Introduction

Layered niobates and titanates exemplified by $K_4Nb_6O_{17}$, $KCa_2Nb_3O_{10}$, $KTiNbO_5$, $K_2Ti_4O_9$, and $Cs_{0.7}Ti_{1.8}O_4$ are known as wide band-gap layered semiconducting oxides that possess intercalating capability and photocatalytic activity [1–3]. They are photoexcited with UV light to form electrons and holes that cause various photocatalytic reactions. Because of their characteristic 2D structures, they exhibit unusual photochemical properties that are not observed for bulk semiconductors such as TiO_2. Typical examples are overall water splitting utilizing the interlayer spaces [4,5] and electron transfer from the oxide layers to the intercalated electron acceptor molecules [6–8].

A recent topic of these materials is exfoliation, by which the layered crystals are delaminated to form single oxide layers called inorganic nanosheets [9]. The nanosheets are obtained as colloidal particles through reactions of the layered crystals with exfoliating reagents (typically tetrabutylammonium ions) in solution systems. The nanosheets are characterized by their extremely high anisotropy (thickness of around 1 nm and lateral dimension up to micrometers) compared with conventional colloidal particles [10,11]. Since the exfoliated nanosheets easily reform layered solids with appropriate techniques such as layer-by-layer assembling, various photoactive nanomaterials have been constructed by restacking the exfoliated niobate and titanate nanosheets [9,12]. Photofunctions observed for these nanoassemblies are photocatalysis [13–15], photoinduced electron and energy transfer [16], photoinduced hydrophilic conversion [17], and photocurrent generation [18]. On the other hand, the exfoliated nanosheets of the layered niobates and titanates can exhibit characteristic photochemical behavior in the colloidal system that is the "as-prepared state" of the nanosheets. Osterloh and coworkers have investigated photocatalytic water decomposition and related reactions by colloidally dispersed niobate nanosheets [2,19–22]. In their systems, large surfaces of the nanosheets have been effectively utilized to show high catalytic activity. Modification of individual nanosheets such as cocatalyst deposition has also been examined.

The colloids of the exfoliated nanosheets of these semiconducting oxides can also be utilized as novel smart colloids which exhibit specific properties that are not realized by the restacked nanoassemblies in solid state based on unusual superstructures derived from the anisotropic shape of the nanosheets [23]. In fact, the "nanosheet colloids" of layered niobates and titanates show liquid crystalline [24–27] and sol–gel [28] phase transitions characteristic to colloidal systems of anisotropic particles. When the exfoliated nanosheets of a niobate and aluminosilicate clay coexist in a colloidal system, a hierarchical superstructure based on morphological dissimilarity of the two nanosheets is obtained. In this system, the niobate and clay nanosheets are phase-separated and

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* Corresponding author. Fax: +81 42 388 7344.
E-mail address: tnakat@cc.tuat.ac.jp (T. Nakato).

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assembled into microdomains, and organic cations are selectively adsorbed on the clay nanosheets [29]. This structure leads to spatial separation of the photocatalytically active niobate nanosheets and functional organic cations selectively adsorbed on the photochemically inert clay nanosheets.

We have recently discovered that the colloidal system consisting hexaniobate and hectorite clay nanosheets and molecular electron acceptor (methylviologen, MV^{2+}) causes efficient and very stable photoinduced charge separation between the niobate nanosheets and the MV^{2+} molecules [30,31]. Also, both the efficiency and stability of the charge separation are controllable over a wide range by the contents of clay nanosheets. The photochemical behavior is ascribed to the spatial separation between the electron donor (niobate nanosheets) and the MV^{2+} molecules, indicating potential applicability of the structured nanosheet colloids of layered niobates and titanates for smart photofunctional systems. However, only the reaction between the niobate and MV^{2+} has been clarified; thus, other examples of photochemical functions should be explored. In addition, reaction control through modification of the colloidal state of the nanosheets such as addition of electrolytes is expected for these systems.

As another photochemical reaction, we have found during the investigation of the mixed colloid system of niobate and clay nanosheets that the colloid shows photoinduced electron accumulation in the niobate nanosheets if MV^{2+} is absent [31]. This reaction is influenced by the clay nanosheets as the charge separation between the niobate and MV^{2+} species. However, the details have been little revealed. Thus, the present paper reports photoinduced electron accumulation in the colloidally dispersed niobate nanosheets and effects of clay and some other molecular additives on the reaction. We indicate that the reaction is principally governed by the clay nanosheets, and that molecular additives give minor effects.

2. Experimental method

2.1. Materials

K_2CO_3, propylammonium hydrochloride, ethylenediaminetetraacetic acid (ETDA) disodium salt, and triethanolamine (TEOA) were purchased from Wako Pure Chemical Co., and used without further purification. Nb_2O_5 was obtained from Soekawa Chemical Co. and used as received. Niobate nanosheets were produced by exfoliation of tetrapotassium hexaniobate $K_4Nb_6O_{17}$ by the method reported previously [10,25]. Briefly, single crystalline $K_4Nb_6O_{17}$ prepared from K_2CO_3 and Nb_2O_5 by a flux method [32] was allowed to react with an aqueous solution of propylamine hydrochloride. This treatment displaced the K^+ ions located between the $[Nb_6O_{17}]^{4-}$ layers for propylammonium ions to delaminate the stacked niobate layers. The exfoliated material was recovered by centrifugation, and the deposit obtained was redispersed in water. The suspension was dialyzed and diluted with water to yield a colloid sample of niobate nanosheets. We call this colloid "niobate colloid" hereafter. Laponite RD, synthetic hectorite clay (ideal formula $Na_{0.7}Si_8Mg_{5.4}Li_{0.4}H_4O_{24}$), was supplied by Rockwood Additives Ltd., and used as received. The cation exchange capacity (CEC) of the clay is 0.075 equivalents per 100 g clay [33]. It was dispersed in water to yield a colloidal sample of clay nanosheets. The lateral dimension of the niobate nanosheets is larger than 1 μm [25], whereas that of Laponite is around 25 nm [34].

A double-component colloid of hexaniobate and hectorite clay, designated as clay–niobate colloid hereafter, was prepared by instantly adding a clay colloid to the niobate colloid. The composition of the standard sample of clay–niobate colloid was [niobate] = 1 g L^{-1} and [clay] = 10 g L^{-1}; the niobate concentration [niobate] is given by the mass of $K_4Nb_6O_{17}$. This composition corresponds to the molar ratio of $[Nb_6O_{17}]^{4-}$:clay = 9.6:75, where the amount of clay is represented by that of the exchangeable cations determined by CEC. The amount of each component was varied in order to examine the influence of the composition on the photochemical behavior. The colloid samples prepared were subjected to photochemical experiments one day after the preparation.

2.2. Observation of the photochemical behavior

A niobate or clay–niobate colloid sample was placed in a water-cooled (25 °C) quartz cell (5 mm in thickness) capped with a rubber septum. After the colloid was bubbled with water-saturated nitrogen gas for more than 30 min, the sample was irradiated by an Ushio SX-UI500XQ 500-W Xe lamp 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 because agitation of the colloid greatly alters the photochemical response.

For comparison, a propylammonium-free suspension of the niobate and clay particles was prepared and irradiated. A niobate colloid was treated with a 6 mol L^{-1} HNO_3 to remove propylammonium ions. Then, the obtained sample was thoroughly washed with water, redispersed in water, and sonicated for 5 h, followed by mixing with a clay colloid. In this product, the niobate was no longer exfoliated but present as ordinary particles consisting of aggregated niobate sheets because of the removal of propylammonium ions that work as the exfoliating agent.

2.3. Analyses

Visible absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer before and after the irradiation. XRD patterns were recorded on a Rigaku Ultima IV diffractometer with a monochromatic Cu Kα radiation. For the XRD measurements, the colloid samples were drop-cast on a glass plate and dried under ambient conditions.

3. Results and discussion

3.1. Appearance of the colloid samples

The colloid samples examined in the present study were all milky and turbid. Fig. 1 shows photographs of the representative samples. Their appearances are almost the same irrespective of the composition. Addition of EDTA did not cause flocculation because of its low concentration (1 mmol L^{-1}). Other additives (propylammonium and TEOA) gave similar colloid appearances (data not shown). The colloidal state was stably kept during experiment, i.e., the UV irradiation and the following spectra recording for 60 min, and no particle settlement was observed after the experiment (the color change is due to the photochemical reaction as described later).

3.2. Structural evaluation of the nanosheets

We performed XRD measurements of the niobate and clay–niobate colloids dried by drop-cast on a glass plate in order to know the conditions of the nanosheets. The XRD patterns indicated that the addition of molecular electron donors did not alter the nanosheet structure of the niobate and clay–niobate colloids. Fig. 2 shows the patterns of the niobate colloid (1 g L^{-1}) with and without the addition of EDTA and TEOA (1 mmol L^{-1}). The XRD pattern of the niobate colloid in the absence of the additives shows the