Intercalation of Metalloporphyrin-Surfactant Complex into Layered Niobate and the Photochemical Injection of Electrons to Niobate

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An anionic metalloporphyrin (Zn(II)TCPP^{4-}) was successfully co-intercalated into the layered oxide $K_4Nb_6O_{17}$ with cationic surfactant (CTAB). Photochemical injection of electrons into the niobate layer was observed.

Layered metal oxide semiconductors (LMOSs) are not only semiconductor but also has layered material properties, including ion exchangeability and large surface area. Two types of interlayers (Interlayer I and II) which have differing properties exist in $K_4Nb_6O_{17}$ (Figure 1).[1] Only limited types of molecules[2] have been intercalated into the interlayer space because of their poor expandability. Metalloporphyrins, which can be applied to many photocatalytic reactions,[3] have never before been intercalated into $K_4Nb_6O_{17}$. In this study, we attempted the intercalation of porphyrin molecule into the layered niobate and found that it was successfully intercalated into the interlayer as a monomer, without aggregation, with cationic surfactant. Cetyltrimethylammonium bromide (CTAB) and tetrakis(4-carboxyphenyl)porphyrinato zinc(II) (Zn(II)TCPP^{4-}) formed an ionic association complex. This complex was found to be easily intercalated into the layered niobate. This is the first example of an intercalation of metalloporphyrin into the layered niobate.

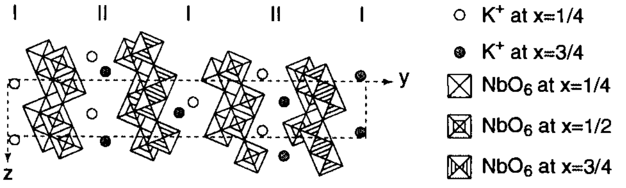

Figure 1. A structure of $K_4Nb_6O_{17}$ having the two interlayer regions.[5]

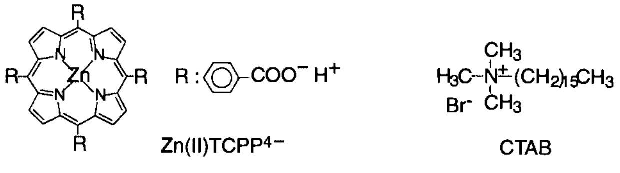

Figure 2. Structures of Zn(II)TCPP^{4-} and CTAB.

$K_4Nb_6O_{17}$ (niobate(K)) and the H$^+$-exchanged niobate (niobate(H)) were used. $K_4Nb_6O_{17}$ was prepared by solid-state reaction reported by Sato[4] et al. K_2CO_3 and Nb_2O_5 were mixed stoichiometrically (2:3) and heated at 1473 K in the air for 20 min in Pt crucible. After grinding, the structure was confirmed by the powder X-ray diffraction pattern[5] (Figure 3a). Niobate(H) was prepared by a sonication of niobate(K) powder in 2 M HCl solution for 100 min. The composition of niobate(H) was determined by EDX analysis to be $H_{2.9}K_{1.1}Nb_6O_{17}$. When 50% of K$^+$ is exchanged to H$^+$, the conduction band edge energy of niobate(K) shifts 0.5V to positive direction (from –0.77 V to –0.26 5V vs NHE).[6] A comparison of the niobate(K) and niobate(H) system is very interesting from the view point of electron transfer from excited Zn(II)TCPP^{4-} (E(P$^+$/P) = 0.80V vs NHE, E^*_S = 2.0 eV).

Intercalation of Zn(II)TCPP^{4-}–CTAB complex into the layered niobate was carried out by stirring the mixture of niobate (5×10^{-5} mol), CTAB (1×10^{-4} mol) and Zn(II)TCPP^{4-} (3×10^{-7} mol) at 333 K for 3 days in 10 mL water. The hybrid compound was filtered with a membrane filter (pore size 0.45 μm) and washed with hot water. As Zn(II)TCPP^{4-} was not detected in the filtrate, Zn(II)TCPP^{4-} was thought to be quantitatively co-intercalated into the interlayer spaces with CTAB. The composition of the niobate–CTAB–Zn(II)TCPP^{4-} hybrid compounds can be estimated by an increment of the weight of the filtrate through the above treatment procedure of intercalation. The compositions were estimated to be niobate(K)–1.3CTAB–0.006Zn(II)TCPP^{4-}, niobate(H)–1.3CTAB–0.006Zn(II)TCPP^{4-} respectively. Their clearance spaces were determined by the powder X-ray diffraction pattern. In the case of the niobate(K)–1.3CTAB–0.006 Zn(II)TCPP^{4-} system, the clearance space was expanded from 0.50 nm (Figure 3a) to 2.70 nm (Figure 3c). The XRD profile of niobate(K)–1.3CTAB–0.006Zn(II)TCPP^{4-} (Figure 3c) was almost the same as that of niobate(K)–1.3CTAB (Figure 3b). These results indicate that porphyrin molecule does not disturb the regular structure formed by $Nb_6O_{17}{}^{4-}$–CTAB.

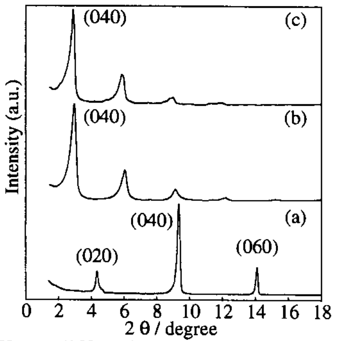

Figure 3. The X-ray diffraction patterns of (a)$K_4Nb_6O_{17} \cdot 3H_2O$, (b)$K_xNb_6O_{17}$ – 1.3CTAB, (c)$K_xNb_6O_{17}$ – 1.3CTAB – 0.006Zn(II)TCPP^{4-}.

From the charge density of niobate (0.128 nm^2 / anion site)[7] and the number of intercalated surfactant molecules, the occupied cross section of CTAB can be estimated. The cation exchangeable site of niobate can be calculated to be 0.512 nm^2 / unit (0.128×4 nm^2). In the case of niobate(K)–1.3CTAB system, the occupied cross section of CTAB was estimated to be 0.39 nm^2 (0.512 / 1.3). Table 1 shows the adsorbed amount of CTAB, the occupied cross section of CTAB and the clearance space (Δd).

Table 1. The structural data of niobate – CTAB hybrid compounds

LMOSs	Adsorbed amount of CTAB(vs anion site of niobate)	Occupied cross section of CTAB / nm^2	Clearance space Δ d^a / nm
$K_4Nb_6O_{17}$	0.33	0.39	2.70
$H_{2.9}K_{1.1}Nb_6O_{17}$	0.33	0.39	2.66

^{a} Δ d = basal spacing – layer thickness (0.41 nm).[7]

The occupied cross section of CTAB was estimated to be 0.39 nm^2 in both niobate(K) and niobate(H) systems. As the cross section of trimethylammonium group is calculated to be 0.36 nm^2,[8] the fact that the occupied cross section of CTAB is almost the same as the cross section of trimethylammonium group indicates that CTAB forms a bilayer structure in the hybrid compound. If single-layer packing of CTAB was formed, the occupied cross section of CTAB would become nearly two times larger than the cross section of trimethylammonium group. From the calculated value of CTAB chain length (2.4 nm), tilt angles of CTAB in the complex were estimated to be 34 degrees with respect to the niobate sheet in both niobate(K)–1.3CTAB and niobate(H)–1.3CTAB systems. Though it is very difficult to know the microscopic orientation of porphyrin, anionic porphyrin can be assumed to exist near the cationic group of CTAB. Figure 4 shows the estimated structure of the niobate–CTAB–Zn(II)TCPP^{4-} hybrid compound.

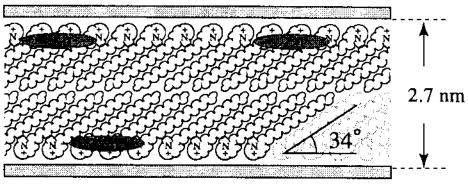

Figure 4. Proposed structure of niobate – CTAB – Zn(II)TCPP^{4-} hybrid compound.

The photochemical behavior of Zn(II)TCPP^{4-} in hybrid compounds was examined. Time-resolved fluorescence spectra of hybrid compounds were measured in benzene at 295 K. In the case of the niobate(K)–1.3CTAB–xZn(II)TCPP^{4-} system (x = 0.006, 0.003, 0.0015), the spectral shape (Figure 5a) was very similar to that of Zn(II)TCPP^{4-} as a monomer in water.

The fluorescence decay curves were analyzed well by single exponential fitting for all concentration of porphyrin in the range of x = 0.006–0.0015. The observed fluorescence lifetimes were 2.3 ± 0.2 ns in all niobate(K)–1.3CTAB systems (x = 0.006–0.0015). These results clearly indicate that the porphyrin exists as a monomer in the narrow space with a height such as 2.7 nm. This is very important from the view point of its utilization for photochemical reactions. In the case of niobate(H)–1.3CTAB–xZn(II)TCPP^{4-} system (x = 0.006, 0.003, 0.0015), the spectral shape (Figure 5b) was similar to that of niobate(K)–1.3CTAB system. Judging from the spectral shape, Zn(II)TCPP^{4-} also exists as a monomer in niobate(H)–1.3CTAB system. However, the fluorescence decay curves could be analyzed as a double exponential curve containing a short lifetime component in all of the porphyrin concentration from x = 0.006–0.0015. Table 2 shows the fluorescence lifetime of intercalated Zn(II)TCPP^{4-} into niobate(H). The relative component ratios (I_1 and I_2) were not affected by the porphyrin concentration from x = 0.006–0.0015. In the case of self-quenching of aggregated Zn(II)TCPP^{4-}, the component ratios would be affected by porphyrin concentration and the different spectral shape should be observed (λ_F = 660 nm). These results indicate that the short lifetime component is not due to self-quenching of aggregated Zn(II)TCPP^{4-}, but suggests an electron transfer from the singlet Zn(II)TCPP^{4-} to niobate layer. The fact that a short lifetime component was observed only in the niobate(H) system which had more positive conduction band energy (–0.265 V vs NHE) than niobate(K) (–0.77 V vs NHE) also supports the electron transfer mechanism. In fact visible light irradiation (λ = 560 nm) for 24 h to niobate(H)(Pt0.3 wt%)–1.3CTAB–0.006Zn(II)TCPP^{4-} in H_2O–CH_3CN (9 : 1) in the presence of KI (1 M) as an electron donor induced an hydrogen evolution (8×10^{-2} μL).

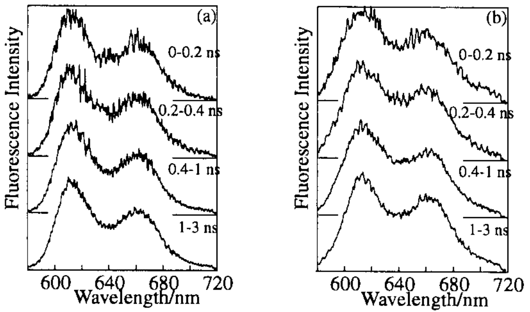

Figure 5. Fluorescence decay curves of (a) niobate(K) – 1.3CTAB – 0.0015Zn(II)TCPP^{4-} and (b) niobate(H) – 1.3CTAB – 0.0015Zn(II)TCPP^{4-} in benzene (excited at 566nm).

Table 2. Fluorescence lifetimes of Zn(II)TCPP^{4-}

Niobate(H)–CTAB–xZnTCPP^{4-}	$\tau_1(I_1{}^a)$/ns	$\tau_2(I_2{}^a)$/ns
x = 0.006	0.28 (0.33)	1.8 (0.67)
x = 0.003	0.20 (0.27)	2.3 (0.73)
x = 0.0015	0.22 (0.34)	2.1 (0.66)

^{a}Relative preexponential term of each component.

In general, an aggregation is induced in narrow space provided by layered material. The most interesting point of our study is that porphyrins co-intercalated with CTAB does not aggregate but does induce electron transfer from the excited monomer porphyrin to the niobate layer. This novel niobate–CTAB–porphyrin system is expected to apply to photocatalytic reactions.

References and Notes

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