The Synthesis of Two Types of Layered Niobate Hybrid Materials by the Selective Intercalation of Ionic Porphyrin

Zhiwei Tong,[†] Tetsuya Shichi,[†] Yoshiyuki Kasuga,[†] and Katsuhiko Takagi*[†,††]

[†]Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Furocho, Chikusa ku, Nagoya 464-8603

[††]CREST, Japan Science and Technology (JST)

$K_4Nb_6O_{17}$ is a layered semiconductor possessing two different layer structures, i.e., interlayers I and II. The present paper reports on the selective synthesis of two types of layered niobate hybrid materials by the introduction of 5,10,15,20-tetrakis(1-methyl-4-pyridinium)-21H,23H-porphyrin ($TMPyP^{4+}$) into either interlayer I or into both I and II by a guest-guest exchange method using the intercalation compounds $(MV^{2+})_xK_{4-2x}Nb_6O_{17}$ and $(PrNH_3^+)_xH_{4-x}Nb_6O_{17}$ as precursors.

Photocatalytic reactions using photofunctional semiconductors have been extensively investigated for their great potential in applications for the conversion of solar energy into useful chemical energy as well as to decompose toxic materials into benign compounds. Among such photocatalytic semiconductors, $K_4Nb_6O_{17}$ possesses a unique layered structure consisting of two different alternatively stacked interlayers I and II, each including hydrated K^+ ions and unhydrated K^+ ions, respectively (Figure. 1).[1] Unhydrated K^+ ions cannot be easily exchanged by other metal ions, in contrast to hydrated K^+ ions which can be directly exchanged.[2] The methyl viologen (MV^{2+})[3] and metal tris(2,2'-bipyridine) complexes, $[M(bpy)_3]^{2+}$ (M = Fe, Ru, Ni),[4] can, thus, be smoothly intercalated into interlayer I of $K_4Nb_6O_{17}$. However, the unhydrated K^+ ions could also be successfully exchanged by incorporating an indirect method using the intercalation compound alkylammonium-$K_xNb_6O_{17}$ as a precursor.[4]
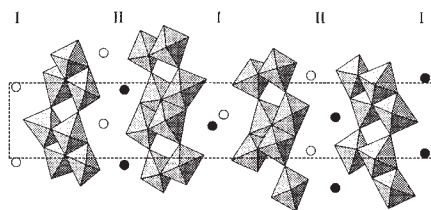

Figure 1. The structure of $K_4Nb_6O_{17} \cdot 3H_2O$ showing the two interlayer regions. Squares represent the NbO_6 octahedra, and the circles indicate the exchangeable cation K^+ within the interlayers.

Inoue et al. have studied the intercalation of a metalloporphyrin complex for layered niobates[5] and along these lines, it can be seen that $K_4Nb_6O_{17}$ layers possessing semiconductive ability can act as an efficient photochemical catalyst and semiconductive host material for the decomposition of water[6] and selective photochemical reactions.[7] In the present paper, we report on the preparation of a novel method of preparing dye-intercalated photofunctional materials by means of a guest-guest exchange technique capable of controlling the guest distribution so as to optimize the photochemical properties. A unique guest-guest ion exchange method was employed in order to synthesize these two different types of intercalated $K_4Nb_6O_{17}$ compounds which could not accommodate $TMPyP^{4+}$ by direct intercalation.

The two types of $(TMPyP^{4+})Nb_6O_{17}$ compounds could be selectively synthesized through ion-exchange with MV^{2+} and $PrNH_3^+$ ions intercalated within the $(MV^{2+})_xK_{4-2x}Nb_6O_{17}$ and $(PrNH_3^+)_xH_{4-x}Nb_6O_{17}$ hybrids as precursors.

The $K_4Nb_6O_{17} \cdot 3H_2O$ employed here was prepared by heating a 2.1 : 3.0 molar mixture of K_2CO_3 and Nb_2O_5 at 1100 °C for 10 h, following the procedures reported by Nassau et al.[8] The obtained powder was then identified by powder X-ray diffraction analysis and compared with existing crystallographic data (Figure 2a). The alternatively layered niobate hybrid with the guest species intercalated only into the interlayers of I is referred to as type-A, while the niobate with the guest species intercalated into both interlayers I and II is referred to as type-B. As the guest ions, MV^{2+} and $PrNH_3^+$ were intercalated into the interlayers of $K_4Nb_6O_{17}$ for the synthesis of two distinct types of $(TMPyP^{4+})Nb_6O_{17}$ compounds, the type-A and B hybrids. The intercalation of MV^{2+} ions into $K_4Nb_6O_{17}$ was carried out by treating $K_4Nb_6O_{17} \cdot 3H_2O$ with an aqueous solution of excess methyl viologen chloride (MV^{2+}), then allowed to stand for three weeks at 70 °C. The intercalation to produce type-A with the $(MV^{2+})_xK_{4-2x}Nb_6O_{17}$ hybrid could be confirmed by powder X-ray diffraction analysis (Figure 2b). The final type-A hybrid $(TMPyP^{4+})_xK_{4-4x}Nb_6O_{17}$ was then prepared by the guest-guest ion-exchange of type-A $(MV^{2+})_xK_{4-2x}Nb_6O_{17}$ with excess $TMPyP^{4+}$ in a glass ampoule for two weeks at 70 °C (Figure 2c).
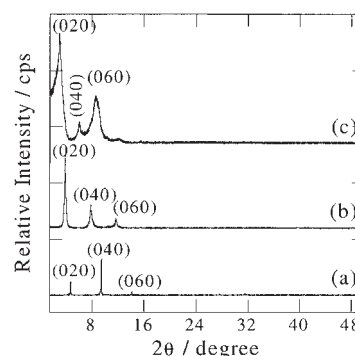

Figure 2. The X-ray diffraction patterns of (a) $K_4Nb_6O_{17} \cdot 3H_2O$, (b) $(MV^{2+})_xK_{4-2x}Nb_6O_{17}$ (type-A precursor), and (c) $(TMPyP^{4+})_{0.2}K_{3.2}Nb_6O_{17}$ (type-A hybrid material).

To synthesize the type-B hybrids, n-propylamine was introduced into the interlayers of I and II by acid-base neutralization with niobic acid (1 g) in a 50 mL aqueous solution of n-propylamine (30% v/v), then allowed to stand for three weeks at 70 °C. The niobic acid $H_4Nb_6O_{17}$ was obtained by keeping the aqueous suspension of the $K_4Nb_6O_{17}$ powder in 6 mol/dm³ HNO_3 for 72 h at 70 °C (100 cm³ HNO_3 per gram $K_4Nb_6O_{17} \cdot 3H_2O$). This procedure was

repeated three times, yielding a white powder, the composition of which was characterized by EDX analysis. The type-B niobate hybrid involing $PrNH_3^+$ ions were characterized by powder X-ray diffraction analysis (Figure 3c). The final type-B niobate hybrid involing $TMPyP^{4+}$, $(TMPyP^{4+})_xH_{4-4x}Nb_6O_{17}$, (Figure 3d) was prepared by a guest-guest ion-exchange of type-B $(PrNH_3^+)_xH_{4-x}Nb_6O_{17}$ with an aqueous solution of excess $TMPyP^{4+}$ in a glass ampoule for two weeks at 70 °C.

Table 1. X-ray powder diffraction data
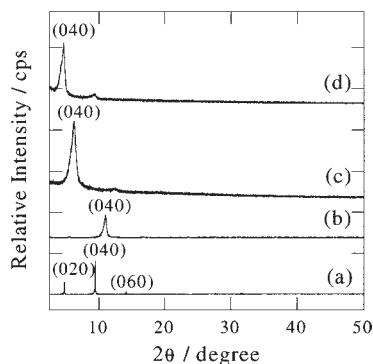
Compound	Type	d_{020}/nm	d_{040}/nm	Δd/nm
$K_4Nb_6O_{17} \cdot 3H_2O$		1.88	0.94	
$K_4Nb_6O_{17}$			0.82	
$(MV^{2+})_xK_{4-2x}Nb_6O_{17}$	A	2.26	1.13	0.62*
$(TMPyP^{4+})_xK_{4-4x}Nb_6O_{17}$	A	2.93	1.46	1.29*
$H_4Nb_6O_{17}$	B		0.81	
$(PrNH_3^+)_xH_{4-x}Nb_6O_{17}$	B		1.57	0.76
$(TMPyP^{4+})_xH_{4-4x}Nb_6O_{17}$	B		1.91	1.10

*The increase in d_{020} from that of $K_4Nb_6O_{17}$ (anhyd).
Δd means the increase in d_{040} from that of $H_4Nb_6O_{17}$.

Figure 3. X-ray diffraction patterns of (a) $K_4Nb_6O_{17} \cdot 3H_2O$, (b) $H_4Nb_6O_{17}$, (c) $(PrNH_3^+)_xH_{4-x}Nb_6O_{17}$ (type-B precursor), and (d) $(TMPyP^{4+})_{0.4}H_{2.4}Nb_6O_{17}$ (type-B hybrid material).

The compositions of the type-A and B niobate hybrids of $(TMPyP^{4+})Nb_6O_{17}$ were measured by combustion analysis, indicating the intercalation of 20% and 40% $TMPyP^{4+}$, respectively, on the basis of the stoichiometry of the niobic acid. The analytical data were as follows: the analytical calculation for the type-A hybrid $(TMPyP)_{0.2}K_{3.2}Nb_6O_{17} \cdot 6.6H_2O$ was C, 8.74; H, 1.72; N, 1.85. Found: C, 8.57; H, 1.75; N, 1.83. For the type-B hybrid Anal. Calc. for $(TMPyP)_{0.4}H_{2.4}Nb_6O_{17} \cdot 11H_2O$ was C, 16.23; H, 3.04; N, 3.44. Found: C, 16.21; H, 2.90; N, 3.55. The calculated C/N molar ratios 5.48 and 5.47 were found to be in good agreement with the theoretical value 5.5, indicating that there remains no detectable amounts of MV^{2+} and $PrNH_3^+$ ions in both the type-A and B hybrids.

The powder X-ray diffraction patterns of type-A with MV^{2+} and type-B with $PrNH_3^+$ are shown in Figures 2 and 3, respectively. The (0k0) reflection peaks showed a marked change after the guest-guest ion-exchange, while keeping the whole profile of the reflection patterns unchanged. In fact, the $TMPyP^{4+}$ hybrid (Figure 2c) retains its type-A layer structure, which is similar to the type-A hybrid $(MV^{2+})_xK_{4-2x}Nb_6O_{17}$ (Figure 2b), as MV^{2+} is intercalated only into interlayers I (type-A precursor). The 2θ angle of the (020) diffraction peaks of type-A, $(MV^{2+})_xK_{4-2x}Nb_6O_{17}$ and $(TMPyP^{4+})_xK_{4-4x}Nb_6O_{17}$, was lower than that of the untreated $K_4Nb_6O_{17} \cdot 3H_2O$. These observations confirm that the interlayer spacings of $K_4Nb_6O_{17} \cdot 3H_2O$ topochemically expand from 2.26 nm to 2.93 nm by its reaction with MV^{2+} and $TMPyP^{4+}$. The basal spacings of $K_4Nb_6O_{17} \cdot 3H_2O$ and their hybrids are shown in Table 1 along with the Δd values. The hydrated potassium niobate, $K_4Nb_6O_{17} \cdot 3H_2O$, exhibits a (020) diffraction peak at 1.88 nm accompanied by an intense (040) peak at 0.94 nm in its XRD pattern (Figure 2a).[8] The d_{020} values corresponding to the sum of two adjacent interlayer spacings are regarded as the basal spacing, the adjacent two interlayers being different from each other owing to the adsorption of water molecules only in interlayers I. On the other

hand, the (020) peak disappears in the XRD pattern of the anhydrous $K_4Nb_6O_{17}$ powder, but the (040) peak appears at 0.82 nm, which is the sum of interlayers I and II. The introduction of $TMPyP^{4+}$ into the layered niobate (type-A) resulted in a ca. 1.29 nm shift in the basal spacing (Δd) compared with the anhydrous $K_4Nb_6O_{17}$. Type-B intercalation of $TMPyP^{4+}$ into the layered niobate resulted in a ca. 1.10 nm shift of the basal spacing (Δd) compared with the niobic acid, $H_4Nb_6O_{17}$. Also, judging from the molecular size of $TMPyP^{4+}$ (ca. 1.73 nm × 1.73 nm),[9] the $TMPyP^{4+}$ molecules were observed to be tilted approximately $\gamma = 49°$ (type-A) and $\gamma = 40°$ (type-B) against the interlayers.

Polarized UV-visible spectroscopic analysis of type-A $(TMPyP^{4+})_xK_{4-x}Nb_6O_{17}$ also confirmed a tilt angle (γ) of 51°, which is in good agreement with that from the XRD measurements. The porphyrin intercalated hybrids of type-A and B were then analyzed by diffuse reflectance spectra in order to observe the interaction of $TMPyP^{4+}$ within the hybrids. The Soret bands of the type-A and B hybrids including $TMPyP^{4+}$ exhibited blue shifts of 17 and 22 nm, respectively, from the bands of the unintercalated $TMPyP^{4+}$ in water, implying that the $TMPyP^{4+}$ molecules are stacked in parallel orientation and interact with each other in a face-to-face manner within the interlayer spaces.[10,11]

In conclusion, two types of unique photofunctional niobate hybrid materials, type-A and B, were successfully synthesised by a guest-guest ion-exchange technique using the intercalation compounds $(MV^{2+})_xK_{4-2x}Nb_6O_{17}$ and $(PrNH_3^+)_xH_{4-x}Nb_6O_{17}$ as precursors. Further studies on their luminescence properties are now underway to on the mechanisms behind host-guest interactions.

References
1 M. Gasperin and M.-T. Le Bihan, *J. Solid State Chem.*, **33**, 83 (1980).
2 K. Kinomura, N. Kumada, and F. Muto, *J. Chem. Soc., Dalton Trans.*, **1985**, 2349.
3 T. Nakato, K. Kuroda, and C. Kato, *J. Chem. Soc., Chem. Commun.*, **1989**, 1144.
4 T. Nakato. K. Kusunoki, K. Yoshizawa, K. Kuroda, and M. Kaneko, *J. Phys. Chem.*, **99**, 17896 (1995).
5 Y. Yamaguchi, T. Yui, S. Takagi, T. Shimada, and H. Inoue, *Chem. Lett.*, **2001**, 644.
6 J. Yoshimura, Y. Ebina, J. Kondo, K. Domen, and A. Tanaka, *J. Phys. Chem.*, **97**, 1970 (1993).
7 Y. I. Kim, S. J. Atherton, E. S. Brigham, and T. E. Mallouk, *J. Phys. Chem.*, **97**, 11802 (1993).
8 K. Nassau, W. Shiever, and J. L. Bernstein, *J. Electrochem. Soc.*, **116**, 348 (1969).
9 E. P. Giannelis, *Chem. Mater.*, **2**, 627 (1990).
10 W. West and S. P. Lovell, and W. Cooper, *Photogr. Sci. Eng.*, **14**, 52 (1970).
11 A. Osuka and K. Maruyama, *J. Am. Chem. Soc.*, **110**, 4454 (1988).