The Hybridization of Layered Niobates with *N*,*N*′-Dimethylbipyridinium Ions by an Acid–Base Reaction

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The hybridization of 1,1′-dimethyl-4,4′-bipyridinium dihydroxide [$MV^{2+}(OH^-)_2$] into $H_4Nb_6O_{17}$ was successfully carried out by a novel neutralization method. X-ray diffraction analysis showed the direct intercalation of the MV^{2+} ions into both of the two chemically different niobate layers in place of the alkylammonium–niobate composite as the precursor.

Photocatalytic reactions by powdered bulk titanium oxide are of interest for their potential in applications for the conversion of solar energy into useful chemical energy as well as for the decomposition of toxic compounds into benign materials. With regard to bulk TiO_2 catalysts, layered metal oxide semiconductors (LMOS) are attractive for their ion-exchange abilities and large surface area. And as one such LMOS, $K_4Nb_6O_{17}$ is especially promising for its unique layered structure. In studies of the intercalation of a metalloporphyrin complex,[1] Inoue et al. have found that $K_4Nb_6O_{17}$ can act as an efficient photochemical catalyst as well as a semiconductive host material for the decomposition of water[2] as well as for other selective photochemical reactions.[3]

As a host material, $K_4Nb_6O_{17}\cdot 3H_2O$ possesses a unique layered structure consisting of alternatively stacked and chemically different layers between which hydrated K^+ ions and unhydrated K^+ ions are included, referred to as interlayers I and II, respectively, as shown in Figure 1.[4] For this composite, the unhydrated K^+ ions cannot be easily exchanged by other metal ions, in contrast to hydrated K^+ ions which can be directly exchanged.[5] However, previous reports[6–8] have shown that, even for the unhydrated K^+ ion, ion exchange is possible by an indirect method using an alkylammonium–niobate composite as a precursor. In this work, we have reported on a novel method of preparing dye-intercalated photofunctional materials by applying an acid–base neutralization technique that led to the direct intercalation of viologen molecules between the niobate layers. We have also investigated the photoinduced electron-transfer reaction for this composite and compared it with existing results.

$K_4Nb_6O_{17}$ was prepared by heating a 3.0:2.1 molar mixture of Nb_2O_5 and K_2CO_3 at 1373 K for 10 h following procedures reported by Nassau et al.[9] The niobic acid ($H_4Nb_6O_{17}$) was obtained by treating the aqueous suspension of the $K_4Nb_6O_{17}$ powder in hydrochloric acid (HCl) for 72 h at room temperature ($10\,cm^3$ of 6 mol/L HCl per gram $K_4Nb_6O_{17}$). This procedure was repeated three times and the composition of the powder was characterized by energy dispersive X-ray analysis.

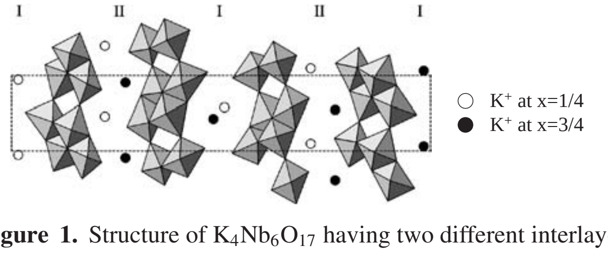

Figure 1. Structure of $K_4Nb_6O_{17}$ having two different interlayers.

Chloride ions (Cl^-) of 1,1′-dimethyl-4,4′-bipyridinium chloride, i.e., methyl viologen ($MVCl_2$), was exchanged by using an anion-exchange resin, as shown in Eq 1. A 137 g portion of an anion-exchange resin (IRA402BL CL, Organo Corp.) was packed into a pyrex glass column ($35\,mm\phi \times 400\,mm$) and treated with excess equivalents of 0.1 M aqueous NaOH solution, and then washed out well three times with ion-exchanged water. $MVCl_2$ (1.5 g) dissolved in 25 mL of ion-exchanged water was filtered through the column and collected to isolate the 1,1′-dimethyl-4,4′-bipyridinium hydroxide ($MV(OH)_2$). This procedure was repeated twice and the remaining Cl^- was monitored by a silver halide reaction.

The niobate–viologen composite was then prepared by introducing the guest molecules $MV(OH)_2$ into the interlayers of $H_4Nb_6O_{17}$ by acid–base neutralization, as shown in Eq 2. The aqueous suspension was prepared by adding 0.2 g of $H_4Nb_6O_{17}$ to 2 mmol/L $MV(OH)_2$ solution and allowing it to stand for 3 h at room temperature. The synthesized composite was then collected by filtering the suspension.

$$MV(Cl)_2 \xrightarrow{(OH^-)} MV(OH)_2, \tag{1}$$

$$\begin{aligned} &H_4Nb_6O_{17} + xMV(OH)_2 \\ &\quad \rightarrow (MV)_xH_{4-2x}Nb_6O_{17} + 2xH_2O. \end{aligned} \tag{2}$$

For a comparative study, the guest molecules $MVCl_2$ were introduced into interlayer I of $K_4Nb_6O_{17}\cdot 3H_2O$ by a conventional ion-exchange technique and $(MV)_yK_{4-2y}Nb_6O_{17}$ was prepared by procedures reported by Tong et al.,[7] as shown in Eq 3

$$\begin{aligned} &K_4Nb_6O_{17} + yMVCl_2 \\ &\quad \rightarrow (MV)_yK_{4-2y}Nb_6O_{17} + 2yK^+Cl^-. \end{aligned} \tag{3}$$

The layered structure of the niobate–viologen composite was investigated by X-ray diffraction (XRD) analysis (Figure 2). The XRD profile of the composite prepared by neutralization (Figure 2c) shows a broad peak assigned to (040) at around $2\theta =$ 5.5 degrees, which is clearly different from the (020) peak which appeared when prepared by the ion-exchange method (Figure 2d). These results indicate that MV^{2+} could be intercalated efficiently into both interlayers I and II of the composite. Neutralization allowed the MV^{2+} to intercalate directly into interlayer II. Moreover, a layered structural change could be observed, as de-

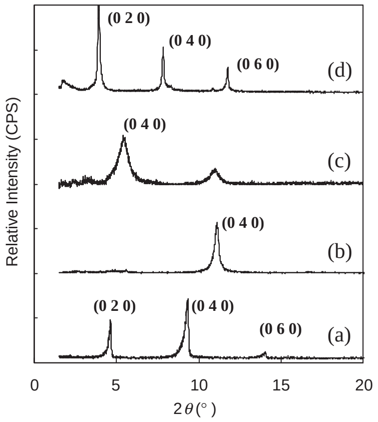

Figure 2. The X-ray diffraction patterns of a) $K_4Nb_6O_{17}\cdot 3H_2O$; b) $H_4Nb_6O_{17}$; c) $(MV)_xH_{4-2x}Nb_6O_{17}$; and d) $(MV)_yK_{4-2y}Nb_6O_{17}$.

Table 1. X-Ray powder diffraction data

Host LMOS	Guest	d_{020}/nm	d_{040}/nm	Δd/nm
$H_4Nb_6O_{17}$			0.81	
$H_4Nb_6O_{17}$	$MV(OH)_2$		1.53	0.72
$K_4Nb_6O_{17}$ (unhyd.)			0.82	
$K_4Nb_6O_{17}\cdot 3H_2O$		1.88	0.94	
$K_4Nb_6O_{17}\cdot 3H_2O$	$MVCl_2$	2.26	1.13	0.62[a]

[a]The increase in d_{020} calculated from that of $K_4Nb_6O_{17}$ (unhyd.).

termined from the spacing changes before and after intercalation, as shown in Table 1. The changes in basal spacing by neutralization was similar to those by ion exchange, indicating the intercalated MV^{2+} ions were also able to retain their original conformation even by the neutralization preparation method.

The photocatalytic reactions were investigated by UV light irradiation (<380 nm) using a 300 W Xenon lamp equipped with a color glass filter U350 (HOYA Corp.). Electron transfers were observed by the formation of $MV^{+\bullet}$, the characteristic peaks of which appeared at around 400 and 600 nm in the UV–vis spectra, as shown in Figure 3, indicating the photocatalytic electron transfer from LMOS to viologen. By comparing the spectral changes in the viologen cation radical before and after UV irradiation, the characteristic peak position and its intensity for the composite by neutralization were similar to those by ion exchange, as shown in Figure 4. These results clearly showed that the new composite, which could intercalate guest ions into both of its interlayers, showed photocatalytic reactions just as efficient as the composite prepared by conventional preparation methods.

In conclusion, the direct hybridization of MV^{2+} into $K_4Nb_6O_{17}$ could be successfully achieved by a novel neutralization technique using $MV(OH)_2$ as the guest molecule and $H_4Nb_6O_{17}$ as the host LMOS. New photofunctional materials can, thus, be prepared without the use of a conventional guest–guest ion-exchange technique and, significantly, could also exhibit photoinduced charge separation between MV^{2+} and $K_4Nb_6O_{17}$ just as efficiently.

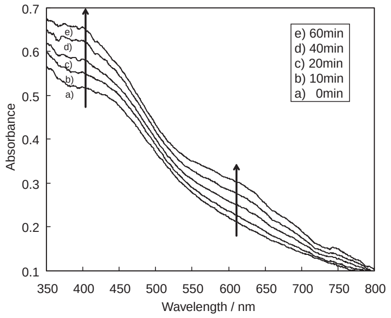

Figure 3. Absorption spectral change of $(MV)_xH_{4-2x}Nb_6O_{17}$ under UV light irradiation.

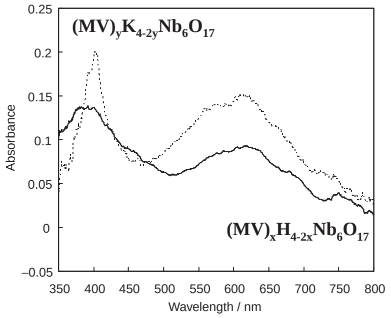

Figure 4. Subtraction spectra before and after UV light irradiation for $(MV)_xH_{4-2x}Nb_6O_{17}$ and $(MV)_yK_{4-2y}Nb_6O_{17}$.

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References

1 Y. Yamaguchi, T. Yui, S. Takagi, T. Shimada, and H. Inoue, *Chem. Lett.*, **2001**, 644.
2 J. Yoshimura, Y. Ebina, J. Kondo, K. Domen, and A. Tanaka, *J. Phys. Chem.*, **97**, 1970 (1993).
3 Y. I. Kim, S. J. Atherton, B. S. Bringham, and T. E. Mallouk, *J. Phys. Chem.*, **97**, 11802 (1993).
4 M. Gasperin and M. T. Le Bihan, *J. Solid State Chem.*, **33**, 83 (1980).
5 K. Kinomura, N. Kumada, and F. Muto, *J. Chem. Soc., Dalton Trans.*, **1985**, 2349.
6 T. Nakato, K. Kusunoki, K. Yoshizawa, K. Kuroda, and M. Kaneko, *J. Phys. Chem.*, **99**, 17896 (1995).
7 Z. Tong, T. Shichi, Y. Kasuga, and K. Takagi, *Chem. Lett.*, **2002**, 1206.
8 Z. Tong, T. Shichi, and K. Takagi, *J. Phys. Chem. B*, **106**, 13306 (2002).
9 K. Nassau, W. Shiever, and J. L. Bernstein, *J. Electrochem. Soc.*, **116**, 348 (1969).

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