Optically Transparent Thin Film of Layered Niobate ($K_4Nb_6O_{17}$) Intercalated with Tris(2,2′-bipyridyl)ruthenium(II)

Zhiwei Tong,*[†] Shinsuke Takagi,[†] Hiroshi Tachibana,[†] Katsuhiko Takagi,[††] and Haruo Inoue*[†,†††]
[†]*Department of Applied Chemistry, Graduate Course of Engineering, Tokyo Metropolitan University,*
1-1 Minami-ohsawa, Hachiohji-city, Tokyo 192-0397
[††]*Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University,*
Furocho, Chikusaku, Nagoya 464-8603
[†††]*CREST, Japan Science and Technology (JST)*

(Received January 28, 2005; CL-050130)

A unique guest–guest ion exchange method was developed for preparing a thin film of a nano-layered $K_4Nb_6O_{17}\cdot 3H_2O$ that possesses both 1) optical transparency and 2) ion-exchangeability, the first example of such a material. An optically transparent $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ hybrid thin film, a potential photo-responsive electrode, was successfully prepared by the guest–guest exchange method by use of the intercalation compound MV^{2+}–$K_4Nb_6O_{17}$ as a precursor.

Layered niobate ($K_4Nb_6O_{17}$) have attracted considerable attention due to their unique structural properties and various applications such as intercalation reactions, photocatalysis, electrochemical responsive materials, ionic exchange processes.[1] Optical transparency is one of the most preferable requisite for those applications. Most layered compounds, however, only serve as optically non-transparent thin film. Methodology on how to prepare the transparent thin films should be one of the most crucial key technology in the field. There are many reports on new composite materials which originate from various layered compounds.[2] Although many of these layered materials have been prepared in the form of thin films, it is very rare that the material retains its ion-exchange capability.[3] Most layered-materials lose their ion-exchangeability when they are in the form of thin films. If films having ion-exchange capability could be obtained, various useful materials with many potential applications could be prepared. Recently, Domen et al. have reported an ion-exchangeable thin film which has been prepared from a suspension of fine particles of $K_4Nb_6O_{17}$.[4] In this paper we report another unique guest–guest ion-exchange method for preparing a thin film of a nano-layered $K_4Nb_6O_{17}\cdot 3H_2O$ that possesses both 1) the optical transparency and 2) ion-exchangeability, in the first example of such a material.

The layered compound, $K_4Nb_6O_{17}\cdot 3H_2O$, employed here was prepared by calcination of a 2.1:3.0 molar mixture of K_2CO_3 and Nb_2O_5 at 1100 °C for 10 h, according to the procedures reported by Nassau et al.[5] Figure 1 shows the layered structure of $K_4Nb_6O_{17}\cdot 3H_2O$. $K_4Nb_6O_{17}$ consists of octahedral units of NbO_6, which form a two-dimensional layered structure via bridging oxygen atoms. The layers are negatively charged, and K^+ ions exist between the layers to compensate for the negative charges of the layers.[6] The intercalation compounds of $K_4Nb_6O_{17}$ with $Ru(bpy)_3{}^{2+}$ are generally very difficult to prepare by a direct reaction because of the bulkiness of $Ru(bpy)_3{}^{2+}$.[7] A two-step intercalation was thus attempted by adopting methylviologen–$K_4Nb_6O_{17}$ intercalation compounds as the intermediates. The methylviologen (MV^{2+}) can be smoothly intercalated into interlayer I of $K_4Nb_6O_{17}$.[8,9] The intercalation of MV^{2+} ions into $K_4Nb_6O_{17}$ was carried out by treating $K_4Nb_6O_{17}\cdot 3H_2O$ (particle size: 2–10 μm) with an aqueous solution of excess methylviologen chloride and then allowing it to stand for three weeks at 70 °C. The MV^{2+}–$K_4Nb_6O_{17}$ hybrid was characterized by thin film X-ray diffraction analysis (Figure 2b). The second step in preparing the $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ thin film electrode was as follows: a 200-μL aqueous suspension of the MV^{2+}–$K_4Nb_6O_{17}$ hybrid was coated onto an ITO (indium tin oxide) glass electrode. The sample was dried at 60 °C for 2 h in air. The area of the formed thin film electrode was about 2 cm^2. $Ru(bpy)_3{}^{2+}$ turned out to be readily intercalated via a guest–guest ion-exchange method into the interlayer of the MV^{2+}–$K_4Nb_6O_{17}$ hybrid thin film via placing the electrode in a 3 mM $Ru(bpy)_3{}^{2+}$ aqueous solutions for 4 days. The thin film obtained by the procedures exhibited a very good optical transparency with a thickness of ca. 15 μm. A photograph of the hybrid thin film is shown in Figure 3. The film showed sufficient stability in aqueous solution or acetonitrile during the electrochemical measurements described later. The optically transparent $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ hybrid thin film electrode was characterized by X-ray diffraction analysis, IR, and UV–vis spectroscopy.

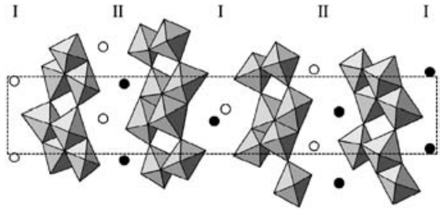

Figure 1. The structure of $K_4Nb_6O_{17}\cdot 3H_2O$ showing the two interlayer regions. Squares represent the NbO_6 octahedra, and the circles indicate the exchangeable cation K^+ within the interlayers.

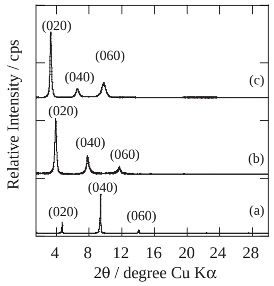

Figure 2. The X-ray diffraction patterns of (a) $K_4Nb_6O_{17}\cdot 3H_2O$, (b) MV^{2+}–$K_4Nb_6O_{17}$ thin film, and (c) $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ thin film.

The starting layered compound, $K_4Nb_6O_{17}\cdot 3H_2O$, was identified by powder X-ray diffraction analysis (Figure 2a). 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, Table 1). The d_{020} values, corresponding to the sum of two adjacent interlayer spacings, are regarded as the basal spacing; these adjacent two interlayers have microenvironments different from each other: water adsorbs only

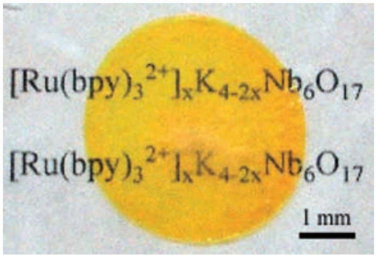

Figure 3. Photograph of $[Ru(bpy)_3{}^{2+}]_xK_{4-2x}Nb_6O_{17}$ hybrid thin film.

Table 1. X-ray diffraction spectrum data

Compound	d_{020}/nm	d_{040}/nm	Δd^a/nm
$K_4Nb_6O_{17}\cdot 3H_2O$	1.88	0.94	
$K_4Nb_6O_{17}$		0.82	
MV^{2+}–$K_4Nb_6O_{17}$	2.26	1.13	0.62
$Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$	2.72	1.36	1.08

[a] Δd means the increase in d_{020} from that of $K_4Nb_6O_{17}$ (anhyd).

in interlayer I. The methyl viologen dication (MV^{2+}) is intercalated only into interlayer I. The 2θ angle of the (020) diffraction peak of MV^{2+}–$K_4Nb_6O_{17}$ was smaller than that of the untreated $K_4Nb_6O_{17}\cdot 3H_2O$ (Figure 2b). The d_{020} was expanded up to 2.26 nm ($\Delta d = 0.62$ nm). The arrangement of the intercalated MV^{2+} ions could be inferred from the Δd values. It has been reported that the intercalation of a flat monolayer MV^{2+} ion into layered materials gives Δd values of 0.28–0.33 nm.[10,11] Therefore, the MV^{2+} ions were suggested to be intercalated with an inclined orientation versus the layer sheet of the interlayer I of $K_4Nb_6O_{17}\cdot 3H_2O$. The introduction of $Ru(bpy)_3{}^{2+}$ into the layered niobate resulted in a ca. +1.08 nm shift in the basal spacing (Δd) compared with the anhydrous $K_4Nb_6O_{17}$ (Figure 2c and Table 1) by the guest–guest ion exchange method. The XRD patterns of $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ as the reaction product maintained a diffraction pattern profile similar to that of the intermediate, MV^{2+}–$K_4Nb_6O_{17}$, even though the positions of the (0k0) peaks changed (Figures 2b and 2c). The basic structure of the intermediate was, thus, concluded to be retained in the intercalation compounds, $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$, i.e., with $Ru(bpy)_3{}^{2+}$ situated in interlayer I only.

The exchange of the MV^{2+} ions by the $Ru(bpy)_3{}^{2+}$ ions was also supported by infrared spectroscopic analysis. The IR spectra of the $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ hybrid exhibited none of the MV^{2+}-related absorption bands observed in the MV^{2+}–$K_4Nb_6O_{17}$ intercalation compound [2962, 2873 (ν_{as} CH_3 and ν_s CH_3); 1640, ν(C–N) of pyridyl group; 1561, ν(C–C) of pyrrole ring], while many absorption bands due to $Ru(bpy)_3{}^{2+}$ were observed. On the basis of the observed C, H, N distribution of 6.54%, 0.68%, and 1.54% for the $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ hybrid, the composition formula for the $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ hybrid was calculated to be $(Ru(bpy)_3{}^{2+})_{0.2}K_{3.6}Nb_6O_{17}\cdot 1.3H_2O$ (10% vs cation exchange capacity), in which the calculated C/N molar ratio, 4.95, is in good agreement with the observed value, 5.00. These results indicate that the MV^{2+} ions are completely removed from the $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ hybrid during the guest–guest exchange procedure.

The $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ hybrid thin film clearly shows the metal–ligand charge transfer (MLCT) band of $Ru(bpy)_3{}^{2+}$ with a spectral shape very similar to that of $Ru(bpy)_3{}^{2+}$ in aqueous solution, except for a 10-nm red shift of the band position. The red shift of the band position for the $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ hybrid thin film may reflect a change of the microenvironment surrounding $Ru(bpy)_3{}^{2+}$.[12]

The cyclic voltammogram (CV) for $Ru(bpy)_3{}^{2+}$ intercalated into the layered niobate $K_4Nb_6O_{17}$ thin film on an ITO electrode is shown in Figure 4. The background current of the layered niobate $K_4Nb_6O_{17}$ thin film without $Ru(bpy)_3{}^{2+}$ on ITO is shown as the dashed line. The typical current-potential curve for $Ru(bpy)_3{}^{2+}$ intercalation into the layered niobate $K_4Nb_6O_{17}$ thin film on ITO is shown as solid line. The shape of the waves is very different from that expected for a surface-confined species, (i.e., symmetrical narrow peaks and anodic and cathode peak separation, ΔE_p, being near zero).[13] Instead, the waves have more diffusive tails. The ΔE_p was 85 mV (at a sweep rate of 30 mV s^{-1}), which is significantly larger than the ≈59 mV found for $Ru(bpy)_3{}^{2+}$ oxidation in solution. A large ΔE_p value usually indicates slow heterogeneous electron transfer.[14] All waves represent one-electron transfers. The voltammetric pattern is characterized, in the positive scan, by one reversible oxidation process (peak system I) and three consecutive reduction steps (peaks II, III, and IV) in the negative scan.

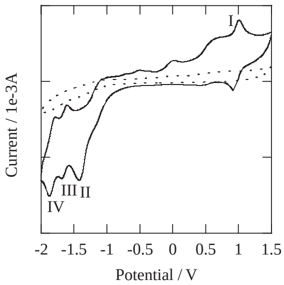

Figure 4. Cyclic voltammograms in CH_3CN, 0.1 M Bu_4NBF_4 for $Ru(bpy)_3{}^{2+}$ intercalation into layered niobate $K_4Nb_6O_{17}$ thin film on ITO (2 cm^2) (solid line) and before intercalation (dashe line). Scan rate, 30 mV/s.

$$[Ru(bpy)_3]^{2+} \rightleftarrows [Ru(bpy)_3]^{3+} + e^- \quad \text{(peaks I)}$$
$$[Ru(bpy)_3]^{2+} + e^- \rightleftarrows [Ru(bpy)_3]^{+} \quad \text{(peaks II)}$$
$$[Ru(bpy)_3]^{+} + e^- \rightleftarrows [Ru(bpy)_3]^{0} \quad \text{(peaks III)}$$
$$[Ru(bpy)_3]^{0} + e^- \rightleftarrows [Ru(bpy)_3]^{-} \quad \text{(peaks IV)}$$

The electrochemical behavior suggests that the optically transparent thin film ($Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ on ITO) would promisingly serve as a good photo-responsive electrode.

The most interesting point of the present study is a developing a guest–guest ion-exchange method to prepare the optically transparent $Ru(bpy)_3{}^{2+}$–$K_4Nb_6O_{17}$ hybrid thin films electrode which can be readily examined by electrochemical methods such as cyclic voltammetry.

This work was supported by the Grant-in-aid for Scientific Research from Japan Society for the Promotion of Science (JSPS) and CREST of the Japan Science and Technology Corp. (JST).

References

1 K. Yao, S. Nishimura, T. Ma, K. Okamoto, K. Inoue, E. Abe, H. Tateyama, and A. Yamagishi, *J. Electroanal. Chem.*, **510**, 144 (2001).
2 M. Ogama and K. Kuroda, *Chem. Rev.*, **95**, 399 (1995).
3 R. Abe, K. Shinohara, A. Tanaka, M. Hara, J. N. Kondo, and K. Domen, *Chem. Mater.*, **10**, 329 (1998).
4 R. Abe, M. Hara, J. N. Kondo, and K. Domen, *Chem. Mater.*, **10**, 1647 (1998).
5 K. Nassau, W. Shiever, and J. L. Bernstein, *J. Electrochem. Soc.*, **116**, 348 (1969).
6 M. Gesperin and M.-T. L. Bihan, *J. Solid State Chem.*, **43**, 346 (1982).
7 T. Nakato, D. Sakamoto, K. Kuroda, and C. Kato, *Bull. Chem. Soc. Jpn.*, **65**, 322 (1992).
8 T. Nakato, K. Kuroda, and C. Kato, *Catal. Today*, **16**, 471 (1993).
9 Z. Tong, T. Shichi, Y. Kasuga, and K. Takagi, *Chem. Lett.*, **2002**, 1206.
10 M. Raupach, W. W. Emerson, and P. G. Slade, *J. Colloid Interface Sci.*, **69**, 398 (1979).
11 O. Poizat, C. Sourisseau, and M. M. Mathey, *J. Chem. Soc., Faraday Trans. 1*, **80**, 3257 (1984).
12 K. Yao, S. Nishimura, Y. Imai, H. Wang, T. Ma, E. Abe, H. Tateyama, and A. Yamagishi, *Langmuir*, **19**, 321 (2003).
13 E. Laviron, *J. Electroanal. Chem.*, **39**, 1 (1972).
14 I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, **103**, 5007 (1981).