A Nanostructured Hybrid Material Synthesized by the Intercalation of Porphyrin into Layered Titanoniobate

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The hybridization of 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)-21H,23H-porphin ($TMPyP^{4+}$) into layered titanoniobate ($KTiNbO_5$), and its structure were studied by means of X-ray diffraction, IR, and polarized and diffuse reflectance UV-vis spectroscopic investigations. The porphyrin molecules incorporated within the intercalation hybrid compound obtained through an intermediary $PrNH_3{}^+$-$TiNbO_5$ hybrid were found to be oriented with a tilt of 46° in a stacked alignment.

Nanostructured materials obtained by the intercalation of porphyrins and metalloporphyrins into two-dimensional matrices have been investigated with the purpose of exploring the photoprocesses[1–8] and catalytic reactions involved.[9,10] Intercalation compounds of layered semiconductors, such as layered titanates and niobates, are able to exhibit unique photochemical and semiconducting properties which allow the intercalation compounds to display a photoinduced host-guest electron transfer,[11,12] in contrast to intercalation compounds of clay minerals. In this study, we have designed a novel intercalation compound of $KTiNbO_5$ with 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)-21H,23H-porphin ($TMPyP^{4+}$), and have also carried out a structural analysis of this new hybrid by means of X-ray diffraction, IR, and polarized and diffuse reflectance UV-vis spectroscopic investigations.

Figures 1 and 2 show the layered structure of $KTiNbO_5$[13] and the molecular structure of $TMPyP^{4+}$, respectively. The metal oxide $KTiNbO_5$ is characterized by a layer structure built up of ($TiNbO_5{}^-$) sheets bound together by K^+ ions with 0.92 nm interlayer spacings, as shown in Figure 1. The ion-exchange properties of the $TiNbO_5{}^-$ layers[14] and the intercalation of aliphatic amines and methylviologen were also investigated.[12,15] The incorporation of bulky ions into the interlayer spaces of titanoniobate is difficult owing the higher charge densities of the $TiNbO_5{}^-$ layers as compared with other layered semiconductors and smectite clays. However, we have successfully incorporated a cationic porphyrin immobilized into layered titanoniobate and also established its structural characteristics.

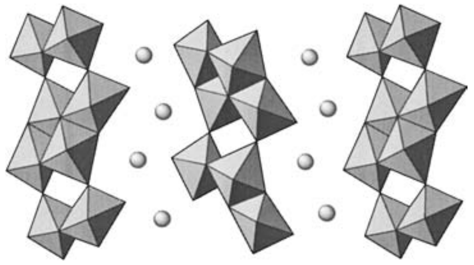

Figure 1. Structure of $KTiNbO_5$. Squares represent the TiO_6 (and NbO_6) octahedra, and circles indicate the exchangeable cation K^+ in the interlayers.

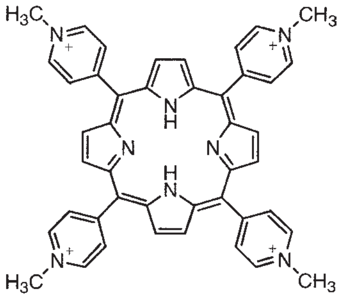

Figure 2. Structural formula of the $TMPyP^{4+}$ ion.

$KTiNbO_5$ was prepared by a conventional solid-state reaction method at 1150 °C for 24 h using K_2CO_3, TiO_2 and Nb_2O_5 as the starting materials. The powder sample was then treated with 2 mol/dm^3 HCl for 24 h three times at room temperature (100 cm^3 HCl per gram potassium titanobiobate). The titanoniobic acid formed was washed with deionized water until free of Cl^-, and then dried in air. Preliminary ion-exchange experiments using K^+ or H^+-exchanged matrices as precursors failed to intercalate the $TMPyP^{4+}$. We finally introduced the propylammonium ions into the $HTiNbO_5$ matrix by neutralization with propylamine, which was then used for the intercalation of the ionic $TMPyP^{4+}$. The titanoniobic acid formed was sealed in an ampoule containing a 50% propylamine aqueous solution (5 cm^3 per gram titanoniobic acid) which was allowed to stand for two weeks at 70 °C. The product was then washed with alcohol and dried in air at 25 °C. The propylammonium titanoniobate ($PrNH_3{}^+TiNbO_5$) was again sealed with a 2.5 mmol/dm^{-3} $TMPyP^{4+}$ aqueous solution and allowed to stand for two weeks at 70 °C. The amount of porphyrin was 2.5 times as much as the ion-exchange capacity of the titanoniobic acid. The resultant product was washed with deionized water until the $TMPyP^{4+}$ absorption could no longer be detected at 425 nm in the filtrate solution. The combustion analysis of the $TMPyP^{4+}$-titanoniobate showed a 36% $TMPyP^{4+}$ ion-exchange with $HTiNbO_5 \cdot 1.8H_2O$ (Anal. Calc. for $(TMPyP)_{0.09}H_{0.64}TiNbO_5 \cdot 1.8H_2O$: C, 15.08; H, 2.40; N, 3.20. Found: C, 15.08; H, 2.50; N, 3.26).

The XRD patterns of $KTiNbO_5$ (Figure 3) indicate that this compound was obtained in a single phase. An exchange of K^+ with proton caused the basal spacing to be shortened to 0.85 nm. The 2θ angle of the (002) diffraction peaks of the hybrid materials, $PrNH_3{}^+TiNbO_5$ and $TMPyP^{4+}TiNbO_5$, were lower than that of $HTiNbO_5$. These observations confirmed that the interlayer spacing of $HTiNbO_5$ was topochemically expanded by the reaction with $PrNH^{3+}$ and $TMPyP^{4+}$. The basal spacing of $HTiNbO_5$ and its intercalation compounds, and the Δd values are shown in Table 1. The insertion of $TMPyP^{4+}$ into the layered

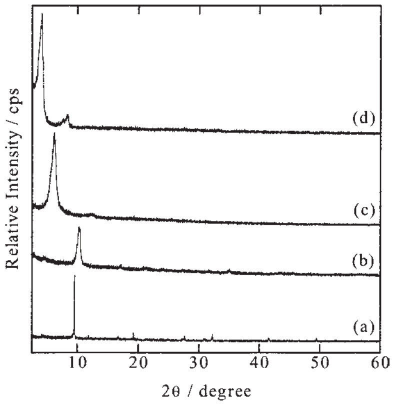

Figure 3. Powder X-ray diffraction patterns of the (a) $KTiNbO_5$, (b) $HTiNbO_5$, (c) $PrNH_3{}^+TiNbO_5$, and (c) $TMPyP^{4+}TiNbO_5$ hybrids.

Table 1. X-ray powder diffraction data

Compound	d_{002}/nm	Δd^a/nm
$KTiNbO_5$	0.92	0.07
$HTiNbO_5$	0.85	0
$PrNH_3{}^+TiNbO_5$	1.57	0.72
$TMPyP^{4+}TiNbO_5$	2.10	1.25

[a] The increase in d_{002} from that of $HTiNbO_5$.

titanoniobate resulted in a shift of the basal spacing (Δd) of about 1.25 nm on the basis of the basal spacing of the protonated titanoniobic acid. An inclination angle (γ) of approximately 46° against the interlayers was estimated on the basis of the gallery height (1.25 nm) and the molecular size of $TMPyP^{4+}$ (ca. 3 nm^2).[16]

The exchange of the propylammonium ions by the $TMPyP^{4+}$ ions could be revealed by infrared spectroscopic analysis (Figure 4). The IR spectra of the product exhibited no absorption bands due to the propylammonium ions of the $PrNH_3{}^+TiNbO_5$ intercalation compound [1507, δ (N–H) of NH_3; 1468, δ (C–H) of CH_2, etc.], although many absorption bands due to $TMPyP^{4+}$ [1640, ν (C–N) of pyridyl substituent; 1563, ν (C–C) of pyrrole ring, 1457 and 1355, ν (C–N) of pyrrole ring, etc.][18] could be observed.

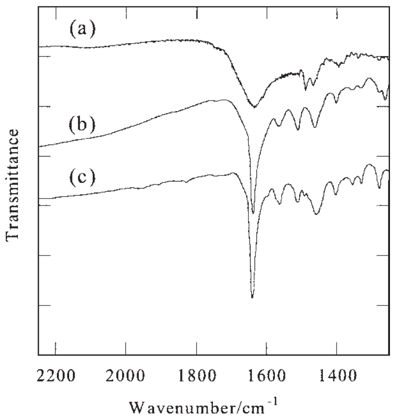

Figure 4. Infrared spectra of (a) $PrNH_3{}^+TiNbO_5$ intercalation compound, (b) $TMPyP^{4+}TiNbO_5$ intercalation compound, and (c) $TMPyP^{4+}$ in KBr.

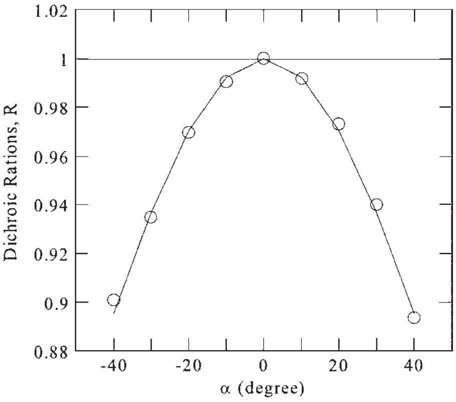

Figure 5. Dependence of the incident angle, α, on the dichroic ratios R of the porphyrin-titanoniobate hybrid thin film.

Figure 5 showed a dependence of an incident light angle upon an intensity of polarized spectroscopy, i.e., a dichroic ratios, from which the tilt angle of $TMPyP^{4+}$ molecules was confirmed to be 47°, in good agreement with the XRD measurements.[17] Such a porphyrin-tilted orientation can also be seen in fluorohectorite clay,[3] zirconium hydrogen phosphate,[5] layered titanate[6] and layered niobate.[7]

The maroon colored porphyrin intercalated titanoniobate has Soret and Q bands showing a blue shift of 16 nm and a red shift of 8–15 nm, respectively, in compared with those of the unintercalated $TMPyP^{4+}$. These results imply 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.[19,20]

In conclusion, a unique nanostructured hybrid material has been successfully synthesised by a cation-exchange method using a $PrNH_3{}^+TiNbO_5$ intercalation compound as the intermediate. The porphyrin was found to be inclined with a tilt angle of 46° within the interlayers of layered titanoniobate.

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