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Synthesis and Spectroscopic and Electrochemical Study on the Intercalation Compound of $KTiNbO_5$ with Cationic Metalloporphyrin

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A cationic metalloporphyrin 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrinatoiron(III), FeTMPyP, was successfully intercalated into layered titanoniobate ($KTiNbO_5$) through a guest-exchange method by using $PrNH_3^+$–$TiNbO_5$ as an intermediate. The characterizations for the intercalation compound FeTMPyP–$TiNbO_5$ were carried out by means of XRD, elemental analysis, and UV–vis absorption spectra. Electrochemical studies reveal that the glass carbon electrode modified with FeTMPyP–$TiNbO_5$ hybrid exhibits good redox activity.

Porphyrins and metalloporphyrins are well known for both biological and catalytic properties. These compounds can be used as homogeneous catalysts or immobilized on various inorganic solids and organic polymers.[1–4] Together, they have attracted increasing interest during the past few decades based mainly on their catalytic properties and many other uses such as electrochemical applications and chemical sensors.

Recently, nanostructured materials obtained by the intercalation of porphyrin derivatives have been investigated with the purpose of exploring photoprocesses and catalytic reactions in the two-dimensional confined media.[5] The layered systems intercalated by porphyrin derivatives have included clay minerals, zirconium hydrogen phosphate, layered metal oxide semiconductors (LMOSs), and layered double hydroxides (LDHs).[6–9] Among them, layered titanates and niobates are fascinating hosts because they are able to exhibit unique photochemical and semiconducting properties which allow the intercalation compounds to display a photoinduced host–guest electron transfer. In the present study, we have successfully prepared FeTMPyP–$TiNbO_5$ hybrid. To the best of our knowledge, this is the first study of metalloporphyrin intercalation into the layered titanoniobate.

Figure 1 gives the structure of $KTiNbO_5$. The direct insertion of FeTMPyP ions is very difficult owing to the bulkiness of FeTMPyP and the higher charge densities of $TiNbO_5^-$ layers. Thus, a guest-exchange method was attempted by adopting $PrNH_3^+$–$TiNbO_5$ as the intermediate.[10]

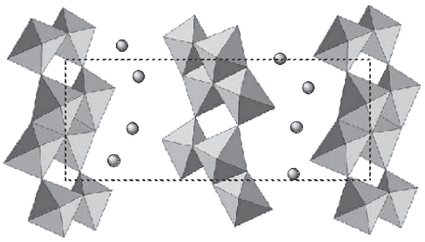

Figure 1. Structure of $KTiNbO_5$. Squares represent the TiO_6 (and NbO_6) octahedra, and circles indicate the exchangable cation K^+ in the interlayer.

$KTiNbO_5$ was synthesized by heating homogeneously mixed powders of K_2CO_3, TiO_2 (anatase, high-purity chemicals), and Nb_2O_5 in molar ratios of 1:2:1 at 1150 °C.[11] The resulting potassium titanoniobate was converted into its protonic phase, $HTiNbO_5$, by treating the powder (1 g) with 80 mL of 2 M HCl solution for 3 days at room temperature, and the HCl solution was renewed every 24 h. Titanoniobic acid formed was centrifuged, washed with copious amounts of distilled water, and then dried in air. 0.5 g of titanoniobic acid was sealed in an ampule with 15 mL of a 50% aqueous *n*-propylamine solution and allowed to stand for two weeks at room temperature. The precipitated powder was washed with alcohol and dried in air. The obtained white powder of propylammonium titanoniobate ($PrNH_3^+$–$TiNbO_5$) was again sealed with 1 mM aqueous solution of FeTMPyP at 50 °C for 3 weeks. The guest exchange was carried out in the dark in order to avoid photodegradation of FeTMPyP. The resultant solution was centrifuged and washed with water thoroughly to obtain the dark brown powder of FeTMPyP–$TiNbO_5$ hybrid.

The XRD pattern of $KTiNbO_5$ (Figure 2a) indicates that this compound is obtained as a single phase. The protonation of $KTiNbO_5$ causes the basal spacing to be shortened to 0.85 nm (Figure 2b). The propylammonium ion-intercalated compound with 1.43 nm of the d_{002} (Figure 2c) is subsequently treated with FeTMPyP to produce a FeTMPyP–$TiNbO_5$ hybrid, resulting in an increase of the d_{002} value to 2.11 nm (Figure 2d). By subtracting the thickness of $TiNbO_5^-$ slab (0.5 nm),[12] the net interlayer height of FeTMPyP–$TiNbO_5$ can be calculated as 1.61 nm. Considering the molecular size of FeTMPyP (1.80 nm × 1.80 nm, estimated by Chem 3D for an optimized structure

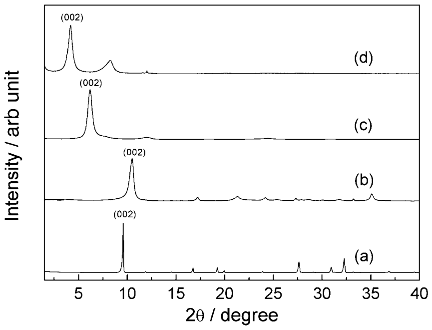

Figure 2. XRD patterns of (a) $KTiNbO_5$, (b) $HTiNbO_5$, (c) $PrNH_3^+$–$TiNbO_5$, and (d) FeTMPyP–$TiNbO_5$.

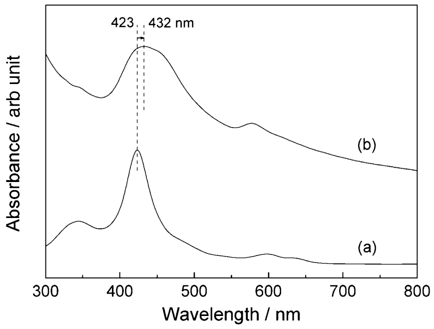

Figure 3. UV–visible absorption spectra of (a) FeTMPyP aqueous solution and (b) the film deposited from FeTMPyP–$TiNbO_5$ hybrid.

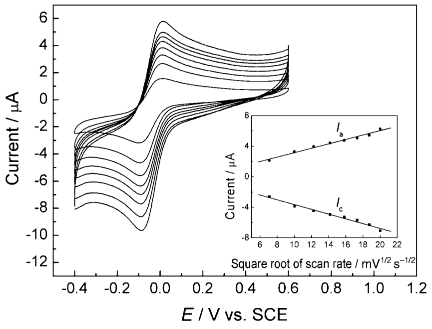

Figure 4. Cyclic voltammograms of thin FeTMPyP–$TiNbO_5$ film in 0.1 M KCl solution at a scan rate of 50, 100, 150, 200, 250, 300, 350, and 400 mV s^{-1}. Inset shows the relationship between peak current and square root of scan rate.

by MM2 calculation), it is postulated here that FeTMPyP forms monolayer coverage with its long molecular axis being tilted approximately 64° against the titanoniobate nanosheets. On the basis of the observed C, H, and N distribution of 14.19%, 2.94%, and 3.05% of the hybrid, the composition formula could be assigned as $(FeTMPyP)_{0.09}H_{0.64}TiNbO_5 \cdot 2.5H_2O$. The area of host layer surface per charge is 0.123 nm^2, so the projected area of each FeTMPyP ion can be calculated as $0.123 \times 1/0.09 = 1.37$ nm^2.[13] The distance between the adjacent Fe centers was calculated as 1.17 nm.

The absorption spectrum of the intercalated system is significantly different from that obtained for an aqueous FeTMPyP solution (Figure 3). The Soret band is broadened and red-shifted to 432 nm. A similar phenomenon has been observed by several groups that have worked with the immobilization of porphyrin and metalloporphyrin onto various inorganic supports.[14–16] Evidently, the electrostatic interaction between FeTMPyP and the titanoniobate surface is a key factor for the interpretation of the variation of absorption spectra. In addition, the steric constraints caused by the support modify the structural arrangement of the porphyrin ring. Close stacking of iron porphyrin ions between the $TiNbO_5^-$ nanosheets enhances the coplanarity between the pyridinium substituents and the porphyrin moiety.

Cyclic voltammograms for the FeTMPyP–$TiNbO_5$ hybrid-modified glass carbon electrode are shown in Figure 4. It is clear that FeTMPyP–$TiNbO_5$ film exhibits very good redox activity in 0.1 M KCl solution. There are a pair of sensitive oxidation/reduction peaks corresponding to $Fe^{III}TMPyP^{5+}/Fe^{II}TMPyP^{4+}$ redox couple.[17] It is also noted that the anodic peak shifts positively and that the cathodic peak shifts negatively with the increment of scan rate from 50 to 400 mV s^{-1}. The inset reveals that the cathodic and anodic peak currents (I_c and I_a) are linearly proportional to the square root of scan rate, suggesting a diffusion-controlled electrode process. Similar electrochemical behavior has also been reported in other layered host–guest systems.[18,19]

In conclusion, the present study has demonstrated for the first time that a cationic metalloporphyrin can be immobilized within the layered titanoniobate, $KTiNbO_5$. The iron porphyrin is found to be tilted with an angle of 64° within the host interlayers. UV–vis spectra suggest that the incorporation of FeTMPyP causes broadening and red shift in the Soret band. The excellent electrochemical activity of the FeTMPyP–$TiNbO_5$ hybrid film has also been proven. Further studies on the catalytic and electrocatalytic properties are now underway in our laboratory.

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