Photoelectrochemical Properties between Nano-sized Layers of Layered Niobate Oxides

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The compounds with a layered structure have interesting chemical properties in such fields as photocatalysis, intercalation, ion-exchange, and photoelectrochemical activity, and their properties change substantially with various kinds of ions and molecules existing in the interlayer. Since layered niobate oxides such as $K_4Nb_6O_{17}$, $KCa_2Nb_3O_{10}$, $CsPb_2Nb_3O_{10}$, and $KTiNbO_5$, show especially high optical activities, they are known to be a typical photocatalyst for the overall decomposition of water into H_2 and O_2. However, those electrochemical properties have hardly been examined. One of those reasons is because a fixation of layered niobate oxides on the electrode was difficult. We have demonstrated that an electrophoretic deposition technique is very useful for preparing the films of layered oxides directly from fine particle suspensions[1].

In this report, the photoelectrochemical redox reactions between the nano-sized layer of the layered niobate oxide films fixed on a conductive substrate are examined. The structure changes of layered niobate oxides caused by the photoelectrochemical reactions are also reported.

Layered niobate oxides ($K_4Nb_6O_{17}$, $KCa_2Nb_3O_{10}$, $Rb_2Nb_3O_{10}$, $KSr_2Nb_3O_{10}$, $CsRb_2Nb_3O_{10}$) were prepared by melting mixtures of various oxide. The final product of those powder were pulverized in a mortar to form a powder with particle sizes of less than about 10 □m**.** The electrophoretic deposition was carried out using the acetone or ethanol suspension containing those powders after ultrasonic wave illumination. The properties of the layered niobate oxide films prepared by electrophoretic deposition were evaluated by CV, UV-VIS, XRD, XPS, and so on. Layered niobate oxides were exfoliated to nanosized two dimensional sheets by treatment with ethylamine and tetrabutyl ammonium hydroxide (TBA). The layered niobate oxide films were also prepared from the exfoliated sheets.

Fig. 1 shows cyclic voltammogram (CV) of the $K_4Nb_6O_{17}$ film deposited on Pt substarte by electrophoretic deposition in 0.1 M K_2SO_4 solution. The CV was measured by irradiating Xe light intermittently on the electrode surface. Since we obtained oxidative photocurrent that occurred due to Xe light irradiation, it was found that the deposited $K_4Nb_6O_{17}$ film showed the nature of the n-type semiconductor. XRD patterns indicated that It was found out from XRD patterns that the films changed from hydrate ($K_4Nb_6O_{17} \cdot 3H_2O$) to unhydrate ($K_4Nb_6O_{17}$) due to the Xe light irradiation. The XRD results of the $K_4Nb_6O_{17}$ films before and after the Xe light irradiation suggested that the anodic photocurrent was caused by the oxidative decomposition of the water between the NbO_6 layers.

Fig. 2 shows CV of the $KCa_2Nb_3O_{10}$ film deposited on Pt substrate by electrophoretic deposition in 0.1 M H_2SO_4 solution that contained 1mM CH_3OH. When potential became more positive than +1.2V vs Ag/AgCl, oxidative current due to oxidation of CH_3OH to HCOOH and HCHO was observed. When potential became more negative than +0.6V, a large anodic photocurrent caused by CO_2 formation on Pt substrate was obtained. The oxidative photocurrent hardly appeared in the dark and increased in more than 200 times in the case of only Pt substrate under Xe light irradiation. This result suggests that electron and hole produced in the $KCa_2Nb_3O_{10}$ film by Xe light irradiation promoted the oxidative reaction on Pt substrate.

Fig. 3 shows that XRD patterns of the $KCa_2Nb_3O_{10}$ films dipped in (a) 0.1M H_2SO_4 (b) 0.1 M methanol, (c) 0.1 M HCHO, and (d) 0.1 M HCOOH solution. The XRD pattern of the film dipped in methanol was almost same as the original film. On the other hand, the (002) peaks corresponding to layer intervals were shifted to low angle in the case of HCHO and HCOOH solution. The expansion of layer intervals indicates that HCHO and HCOOH intercalated into the layers of the $KCa_2Nb_3O_{10}$ films. Thus, this result suggests that photoelectrochemical oxidation to CO_2 from HCHO and HCOOH took place selectively between the layers.

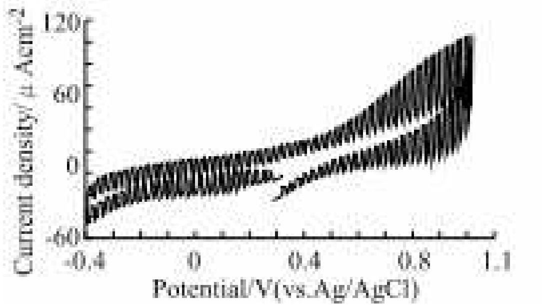

Fig.1 CV of $K_4Nb_6O_{17}$ film irradiated with Xe light intermittently in 0.1M K_2SO_4 solutoin

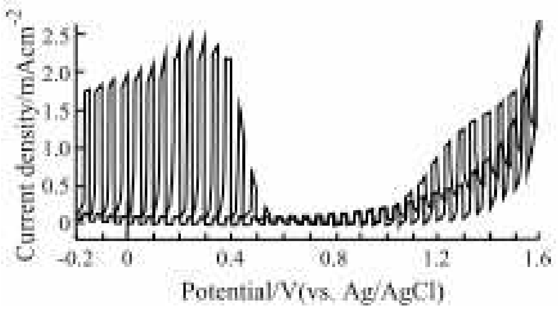

Fig.2 CV of $KCa_2Nb_3O_{10}$ film irradiated with Xe light intermittently in 0.1M H_2SO_4 + 1mM CH_3OH solutoin

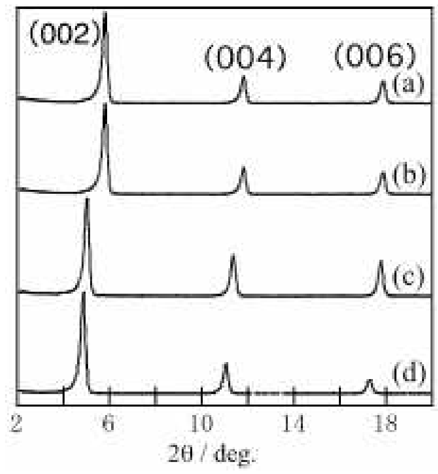

Fig. 3 shows that XRD patterns of the $KCa_2Nb_3O_{10}$ films dipped in (a) 0.1M H_2SO_4 (b) 0.1 M methanol, (c) 0.1 M HCHO, and (d) 0.1 M HCOOH solution.

1) M.Koinuma et al. J. Electroanal. Chem. 531 81-85 (2002).