

New Tantalum Oxynitride Photocatalyst

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Hydrous layered perovskite oxynitride, $K_2LaTa_2O_6N \cdot xH_2O$, as new tantalum oxynitride photocatalyst, was prepared. The prepared oxynitride was characterized using powder x-ray diffraction, thermogravimetric analysis, UV-Vis spectroscopy and X-ray photoelectron spectroscopy. The oxynitride exhibited high photocatalytic performance and the progress of photocatalytic H_2O decomposition was confirmed under UV irradiation without combining any co-catalysts.

Key words: Photocatalyst, Tantalate, Layered Perovskite, Hydration, Intercalation

1. INTRODUCTION

Many oxide-based photocatalysts have been developed for water splitting under UV light irradiation. Although some tantalates such as NiO-loaded $Sr_2Ta_2O_7$ [1] and $NaTaO_3 \cdot La$ [2] decompose water with high quantum efficiency under UV irradiation. Recently, we have been studying layered perovskite containing tantalum as new efficient photocatalysts [3,4]. The layered perovskite tantalates with hydrated interlayer space, $A_2SrTa_2O_7 \cdot nH_2O$ ($A = H, K, \text{ and } Rb$), showed higher photocatalytic activity than that of anhydrous $Li_2SrTa_2O_7$.

However, the absorption of sunlight is expected to be inefficient because of the wide bandgap. In these Ta-based oxides, the wide bandgap is due to a deep position of a valence band consisting of O 2p orbitals. Recently, Domen et al. have been reported transition (oxy)nitrides as new visible light driven photocatalysts [5,6]. Based on the band structure calculation of TaON, the bottom of the conduction band is based on empty Ta 5d orbitals and the top of the valence band consists of a hybridization of N 2p and O 2p orbitals. The position of the valence band with hybridized orbital is higher than that of the pure oxide, resulting in narrow band gap energy (2.5 eV) to absorb the sun light. Therefore, the tantalum nitride and oxynitride are promising candidates for visible light driven photocatalysts.

In this paper, we reported the first successful example of layered perovskite-type oxynitride tantalate with hydrated interlayer space, $K_2LaTa_2O_6N \cdot xH_2O$. The photocatalytic activity of the novel catalyst to H_2O decomposition was compared to that of oxide material.

2. EXPERIMENTAL

The layered perovskite-type oxynitride tantalate $K_2LaTa_2O_6N$ was prepared by two-step firing synthesis. The precursor $K_2La_{2/3}Ta_2O_7$ powder was synthesized by a conventional solid state reaction. Stoichiometric amounts of La_2O_3 and Ta_2O_5 with a 167 % molar excess of K_2CO_3 were mixed together and heated in air at 1123 K for 6 h and then 1573 K for 8 h. $K_2LaTa_2O_6N$ was prepared by heating a mixed powders with a ratio of $K_2La_{2/3}Ta_2O_7 : La_2O_3 = 1 : 1/6$ in an atmosphere of flowing NH_3 at 1173 K for 1 h.

The crystal structure of the obtained samples was examined by X-ray diffraction (MAC Science; MX Labo) with Cu K α radiation (40 kV, 25 mA) at room temperature. Thermal analysis (TG/DTA) was made using MTC1000 (MAC Science) operating with a heating rate of 10 K/min. Diffuse reflectance spectra were measured with a UV-Vis spectrometer (Jasco; V-550). The optical band-gap energy was calculated from onset of absorption edges. The photocatalytic decomposition of water was performed in an inner irradiation cell made of quartz with a gas-closed circulating system. The catalyst powder (0.5 g) was dispersed in 200 ml of pure water by a magnetic stirrer. The light source was a 400 W high-pressure mercury lamp. Before the reaction, the mixture was degassed completely and then Ar (ca. 15 kPa) was introduced. The evolved gases were collected to the sampler (3 ml), directly connected to the closed gas circulation system to avoid any contamination from air and analyzed by gas chromatograph (Hitachi, TCD, molecular sieve 5A column and Ar carrier).



Fig. 1 Photograph of oxynitride $K_2LaTa_2O_6N \cdot xH_2O$ powder.

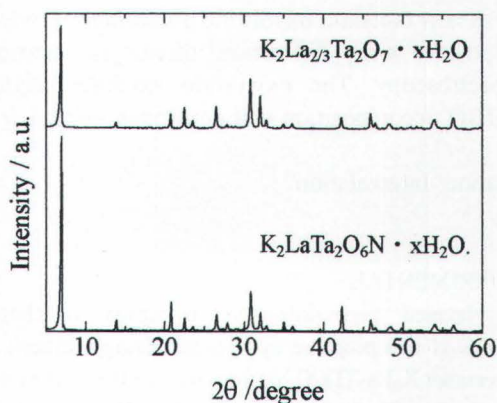


Fig. 2 Powder X-ray diffraction patterns of $K_2La_{2/3}Ta_2O_7 \cdot xH_2O$ and oxynitride $K_2LaTa_2O_6N \cdot xH_2O$ powder.

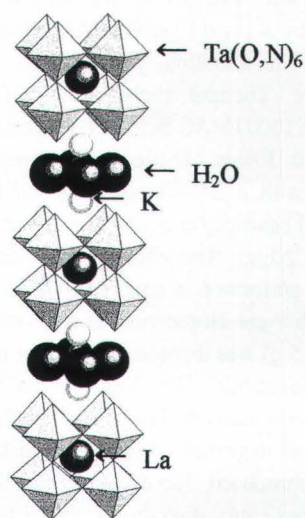


Fig. 3 Structural model of $K_2LaTa_2O_6N \cdot xH_2O$.

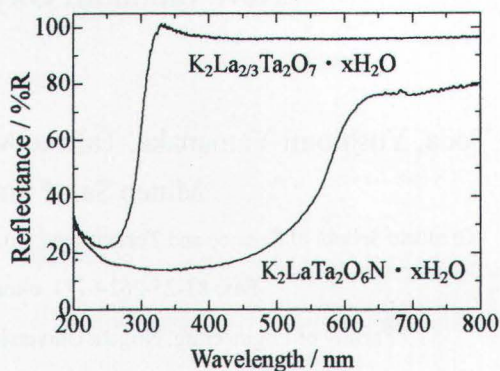


Fig. 4 Diffuse reflectance UV spectra of $K_2La_{2/3}Ta_2O_7 \cdot xH_2O$ and $K_2LaTa_2O_6N \cdot xH_2O$ powder.

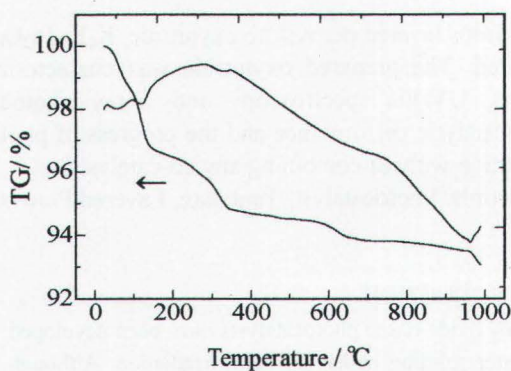


Fig. 5 TG/DTA profiles of $K_2LaTa_2O_6N \cdot xH_2O$.

3. RESULTS AND DISCUSSION

The photograph of the prepared oxynitride in this work is shown in Fig. 1. As shown in Fig. 1, the oxynitride powders display a reddish brown color and this is different from the oxide sample. The powder X-ray diffraction patterns of the samples are shown in Fig. 2. The XRD pattern of oxynitride is noticed to be exactly similar to that of oxide $K_2La_{2/3}Ta_2O_7 \cdot xH_2O$ in the literature [7]. Figure 3 represents a structural model of $K_2LaTa_2O_6N \cdot xH_2O$. The structure of the oxynitride sample can be described as formed from two $Ta(O,N)_6$ octahedra thick slabs of a perovskite lattice. The adjacent layers are stacked immediately above each other in the same arrangement. UV diffuse reflectance spectra of the catalysts are shown in Fig. 4. The oxide sample has an absorption band in the ultraviolet region and shows a clear absorption edge at around 320 nm. The band gap of $K_2La_{2/3}Ta_2O_7 \cdot xH_2O$ was about 3.9 eV from the absorption edge. On the other hand, the absorption band-edge of $K_2LaTa_2O_6N \cdot xH_2O$ is at *ca.* 600 nm. The absorption edge of oxynitride is shifted by about 280 nm from that of oxide sample and the band gap energy can be estimated to be 2.1 eV. The dehydration behaviour of $K_2LaTa_2O_6N \cdot xH_2O$ was studied by TG/DTA analysis. The result in Fig. 5 shows a distinct loss of water and

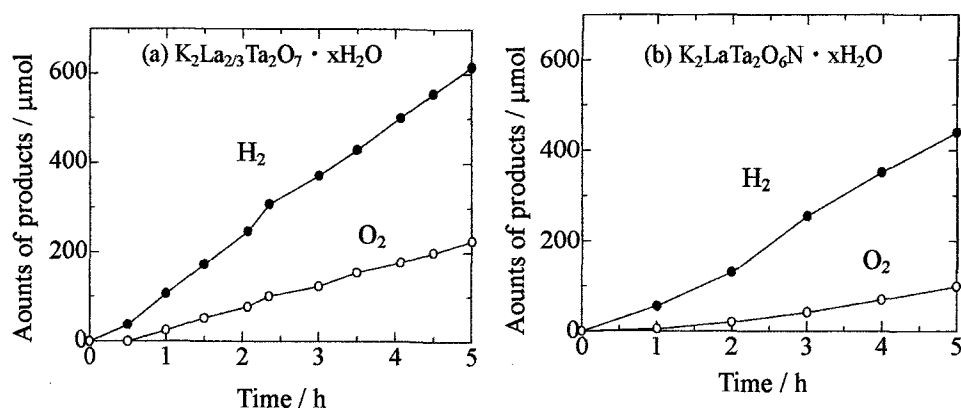


Fig. 6 H_2 and O_2 evolutions from distilled water over (a) $K_2La_{2/3}Ta_2O_7 \cdot xH_2O$ and (b) oxynitride $K_2LaTa_2O_6N \cdot xH_2O$ powder. Catalyst amount is 0.5 g.

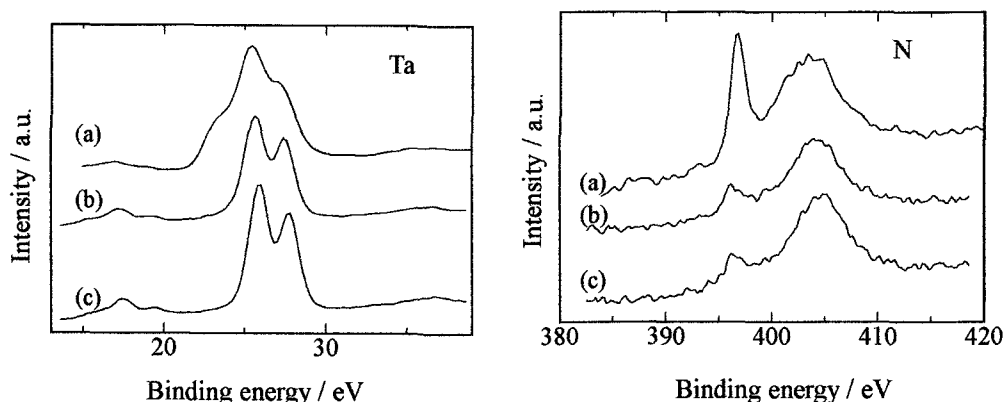


Fig. 7 XPS spectra of (a) TaON, (b) oxynitride $K_2LaTa_2O_6N \cdot xH_2O$ and (c) $K_2La_{2/3}Ta_2O_7 \cdot xH_2O$.

nitrogen at a temperature range of $373\text{ K} < T < 900\text{ K}$, which is attributable to the transformation of hydrate to anhydrous layered material and decomposition of oxynitride.

Fig. 6 shows the evolution H_2 and O_2 in the photocatalytic decomposition of water over $K_2LaTa_2O_6N \cdot xH_2O$ without any catalyst pretreatment. The oxynitride material produced H_2 and O_2 simultaneously, though the rate of O_2 evolution was less than the stoichiometric amount. $K_2LaTa_2O_6N \cdot xH_2O$ (initial rate of H_2 evolution ($90\ \mu\text{mol/h}$)) showed slightly low activity for water decomposition as compared to the $K_2La_{2/3}Ta_2O_7 \cdot xH_2O$ ($110\ \mu\text{mol/h}$). No N_2 evolution was detected. The degradation of $K_2LaTa_2O_6N \cdot xH_2O$ did not occur during the photocatalytic water decomposition. We also studied the reaction over the anhydrous perovskite $KTaO_3$ and layered perovskite $Li_2SrTa_2O_7$. These materials showed moderate activity for H_2 evolution ($KTaO_3$ $25\ \mu\text{mol/h}$; $Li_2SrTa_2O_7$ $30\ \mu\text{mol/h}$). This

suggests that the hydrous layered oxynitride, $K_2LaTa_2O_6N \cdot xH_2O$, was highly effective than anhydrous tantalates, $KTaO_3$ and $Li_2SrTa_2O_7$. Therefore, the presence of hydrated interlayer space is important for improving the photocatalytic activity of Ta-based oxide and oxynitride photocatalysts [3,4]. Recently, Machida *et al.* reported that the photocatalytic reaction of water decomposition proceeds at interlayers of the hydrated layered perovskites based on a radioisotope experiment [8]. In the case of hydrous tantalates, the photogenerated electrons and holes may be easily transferred to the interlayer and thus the water in the interlayer space can be effectively decomposed [9].

The sample was also characterized by x-ray photoelectron spectroscopy (XPS). Fig. 7 shows the preliminary XPS result for the Ta and N atoms. Two Ta peaks are correspondence to Ta $4f_{7/2}$ and Ta $4f_{5/2}$ spin orbital splitting. The binding energies of the oxynitride $K_2LaTa_2O_6N$ were observed between the oxide

$K_2La_{2/3}Ta_2O_7$ and the oxynitride TaON. This shift in the binding energy suggests the bonding between Ta and N in the oxynitride $K_2LaTa_2O_6N$.

4. CONCLUSIONS

In summary, we have developed novel oxynitride photocatalyst $K_2LaTa_2O_6N \cdot xH_2O$ with hydrated layered perovskite structure. The catalyst without any modification showed high photocatalytic activity. This is the first successful example of highly active oxynitride tantalate photocatalyst with hydrated interlayer space. The photocatalytic water decomposition under visible light irradiation is currently under investigation.

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