

Black-colored nitrogen-doped calcium niobium oxide nanosheets and their photocatalytic properties under visible light irradiation

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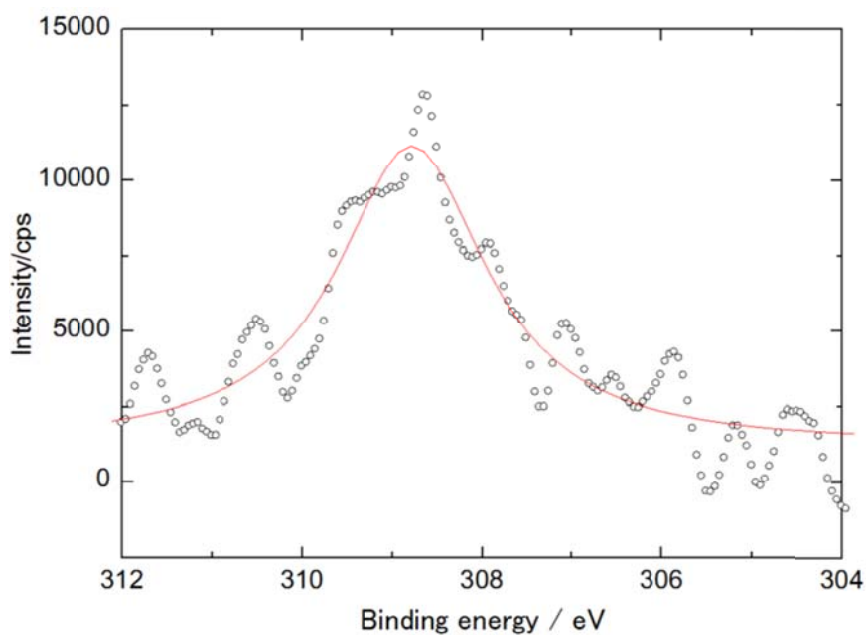


Fig. S-1 X-ray photoelectron spectroscopy (XPS) Rh 3d5/2 narrow spectrum for RhO_x(1wt.%) -loaded Ca₂Nb₃O_{10-x}N_y nanosheet (X-ray photoelectron spectroscopy: Shimadzu AXIS 165). The Rh 3d5/2 peak was 308.7 eV, which is close to Rh species on Rh₂O₃-loaded Ca₂Nb₃O₁₀ nanosheet (309.3 eV) [S-1]. The loading condition of Rh species on RhO_x(1wt.%) -loaded Ca₂Nb₃O_{10-x}N_y nanosheet might be +3(Rh₂O₃).

[S-1] H. Hata, Y. Kobayashi, V. Bojan, W. J. Youngblood, T. E. Mallouk, *Nano Lett.*, 2008, **8**, 794.

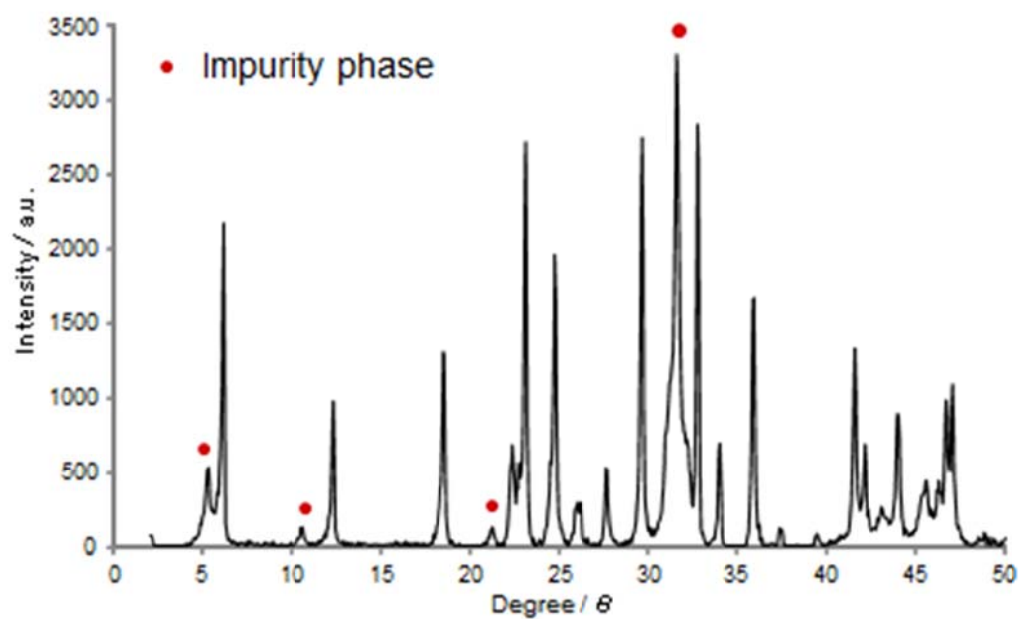


Fig. S-2. XRD pattern of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ after calcination at 900 °C under NH_3 flow. Red circles shows impurity phase, which could not be assigned. In terms of calcination temperature, when $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ was prepared at 700 °C, the sample contained white-colored powder and black-colored powder. The sample prepared at 800 °C had no impurity phase, and the color was homogeneous. Therefore, we prepared sample at 800 °C

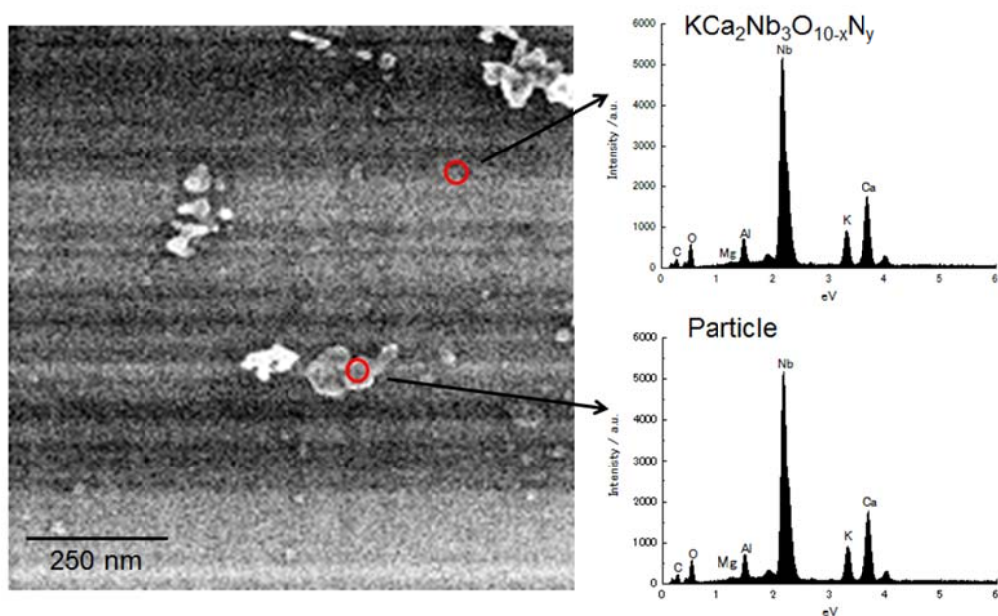


Fig.S-3 SEM image and EDX spectra of $\text{KCa}_2\text{Nb}_3\text{O}_{10-x}\text{N}_y$ surface. Although the particles were observed in SEM image, there was no difference in chemical composition between the particle and $\text{Ca}_2\text{Nb}_3\text{O}_{10-x}\text{N}_y$. Probably, the composition of the small particle was close to that of $\text{KCa}_2\text{Nb}_3\text{O}_{10-x}\text{N}_y$. However, in this study, we could not clear the chemical composition and structure of the impurity phase.

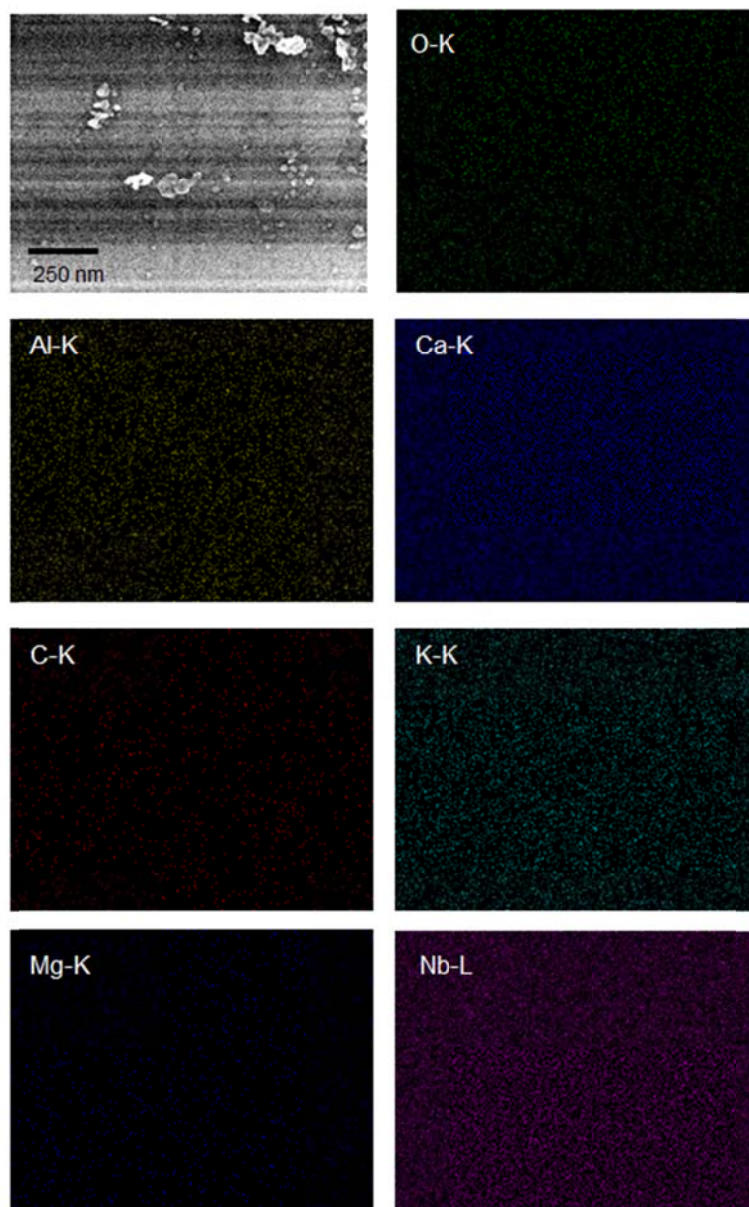


Fig.S-4 SEM image and EDX mapping image of $\text{KCa}_2\text{Nb}_3\text{O}_{10-x}\text{N}_y$ surface. Although the particles were observed in SEM image, there was no difference in chemical composition between the particle and $\text{Ca}_2\text{Nb}_3\text{O}_{10-x}\text{N}_y$.

Table S-1. The degree (2 theta) and the d value of the main peaks of the ICSD crystallographic data of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ (#91098) and $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ prepared in this study.

(hkl)	$\text{KCa}_2\text{Nb}_3\text{O}_{10}$ [reference data ^{a)}]		$\text{KCa}_2\text{Nb}_3\text{O}_{10}$ prepared in this study	
	2theta / °	d / nm	2theta / °	d / nm
(0 2 0)	5.99	1.4754	6.02	1.4679
(0 4 0)	11.99	0.7377	12.05	0.7339
(0 6 0)	18.02	0.4918	18.12	0.4893
(0 0 2)	23.04	0.3857	23.21	0.3829
(1 1 0)	23.10	0.3847	23.31	0.3813
(0 2 2)	23.83	0.3732	24.00	0.3705
(0 8 0)	24.11	0.3688	24.23	0.3670
(1 3 0)	24.64	0.3609	24.86	0.3579
(0 4 2)	26.05	0.3418	26.23	0.3395
(1 5 0)	27.49	0.3242	27.71	0.3217
(0 6 2)	29.41	0.3035	29.60	0.3016
(1 7 0)	31.31	0.2855	31.54	0.2834
(1 1 2)	32.85	0.2724	33.13	0.2702
(1 7 1)	33.44	0.2677	33.69	0.2658
(0 8 2)	33.59	0.2666	33.80	0.2649
(0 14 0)	42.87	0.2108	43.10	0.2097
(2 0 0)	46.79	0.1940	47.24	0.1923
(0 0 4)	47.08	0.1929	47.45	0.1915
(0 14 2)	49.22	0.1850	49.52	0.1839

a) Fukuoka, H.; Isami, T.; Yamanaka, S. *J. Solid State Chem.* (2000), 151, 40.

Unit Cell: a=0.38802(9), b=2.9508(6), c=0.7714(1) nm

Space Group: C m c m

SG Number: 63

Experimental details:

Preparation of nanosheet:

$\text{KCa}_2\text{Nb}_3\text{O}_{10}$ powder was prepared by a solution method. KOOCCCH_3 , $\text{Ca}(\text{OOCCCH}_3) \cdot 0.5\text{H}_2\text{O}$, and Nb_2O_5 were mixed at a ratio of 1.3:2:3 in water, after which the water was evaporated by heat treatment. The mixture was calcined in air at 673 K for 2 h, followed by grinding and calcination at 1473 K for 10 h. $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ was converted into $\text{KCa}_2\text{Nb}_3\text{O}_{10-x}\text{N}_y$ by calcination at 800 °C under NH_3 flow. The K ions in the $\text{KCa}_2\text{Nb}_3\text{O}_{10-x}\text{N}_y$ were exchanged with protons by acid exchange with 5M HNO_3 solution for a week. The protonated form was stirred for one week in 150 mL of a 0.025 M tetrabutylammonium hydroxide (TBAOH) aqueous solution to exfoliate into nanosheets. The separation of unexfoliated powder was performed by spontaneous precipitation for 1 day and the supernatant was used as a nanosheet suspension. $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ nanosheet was prepared from $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ powder, in the same way as $\text{Ca}_2\text{Nb}_3\text{O}_{10-x}\text{N}_y$ nanosheet.

Photocatalytic reactions:

A photocatalytic reaction was performed using a conventional closed circulation system. A quartz reaction cell was irradiated by light from an external light source (500 W Xe lamp). During the reaction, the suspension was mixed using a magnetic stirring bar. Ar gas (initial pressure: 18.3 kPa) was used as the circulating carrier gas. Co-catalyst (Rh:1wt.%) was photodeposited on the nanosheets in 20 vol.% methanol aqueous solution (100 mL of nanosheet suspension, 40 mL of methanol, 30 mL of water) containing $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (99.5%, Wako) by irradiation with the 500 W Xe lamp for 12 h. The amounts of H_2 and O_2 formed were measured by gas chromatography with a thermal conductivity detector, which was connected to a conventional volumetric circulating line by a vacuum pump. 200 mL of water, 0.1 M AgNO_3 aqueous solution, or 20 vol.% methanol aqueous solution was used as the reaction solution. A cellophane tube filled with 0.01 M H_2SO_4 aqueous solution was immersed in the nanosheet suspension while stirring constantly. This resulted in nanosheet deposition due to proton absorption. The deposited nanosheets were washed in several changes of water by centrifugation to remove residual TBAOH. The nanosheet paste obtained by centrifugation was used without drying for photocatalytic activity evaluations. In the case of photocatalytic hydrogen evolution test from methanol aqueous solution, the photocatalytic activity was evaluated using the nanosheet suspension used for loading the co-catalyst without any change.