Electronic Supplementary Information

Synergetic photocatalytic hydrogen evolution over oxide nanosheets combined with photochemically inert additives

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Experimental details

(1) Sample preparation

A colloid of the niobate nanosheets, where negatively charged niobate ($Nb_6O_{17}^{4-}$) nanosheets accompanied by propylammonium ions as the countercations, was prepared by the method reported previously.[1] Single crystalline $K_4Nb_6O_{17}$ was prepared by a flux method; a mixture of K_2CO_3 (Wako Pure Chemical Industries, Ltd., Japan) and Nb_2O_5 (Soekawa Chemicals Co., Ltd., Japan) was heated at 1150 °C and gradually cooled.[1-2] $K_4Nb_6O_{17}\cdot 3H_2O$ (1 g) was treated with a 0.2 mol L^{-1} aqueous solution of propylammonium chloride (Tokyo Chemical Industry Co., Ltd., Japan) at 120 °C for a week to exchange the interlayer potassium ions for propylammonium ions.[1, 3] The reaction product was centrifuged at 11000 rpm, washed, and dialyzed with water to yield the stock sample of the niobate nanosheet colloid (~2 g L^{-1}). A colloid of the niobate nanosheets with smaller lateral sizes was prepared by ultrasonic treatment of the stock sample for 4 h.

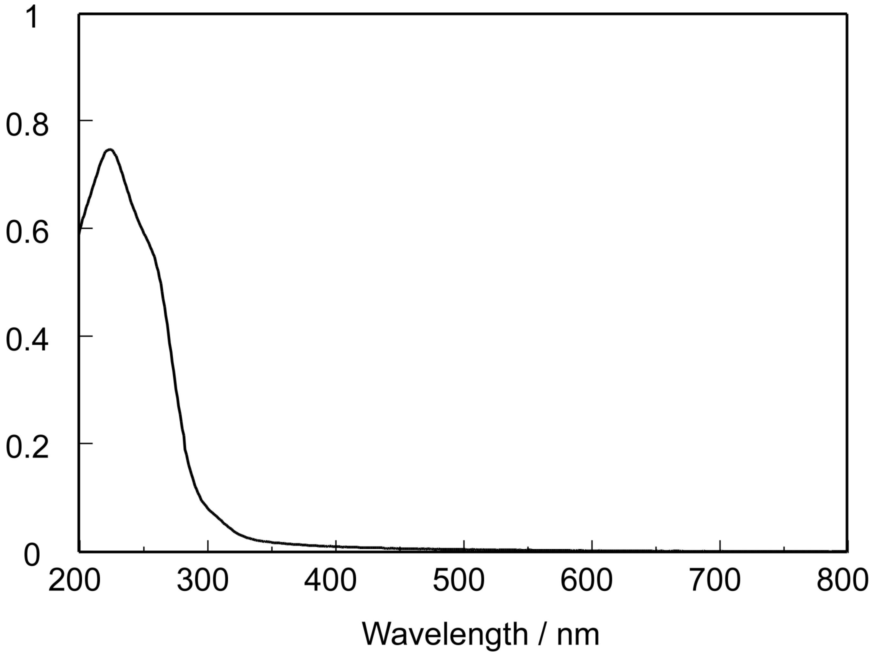
Pt cocatalyst was loaded on the niobate nanosheets by photodeposition. An H_2PtCl_6 aqueous solution was added to the niobate nanosheet colloid, and then a 50 mL portion of the colloid was introduced into a Pyrex optical cell for light irradiation. The colloid was irradiated by a 250 W high-pressure Hg lamp for 15 min to deposit Pt nanoparticles on the nanosheets after bubbling with N_2. Details of the UV irradiation are described later. The Pt-deposited niobate nanosheets were centrifuged and redispersed in water.

A clay colloid was prepared by dispersing powdery synthetic hectorite clay (Laponite RD, supplied by Rockwood Additives Ltd.). In this colloid, clay layers were delaminated to form silicate nanosheets. Loading of Pt cocatalyst on the clay nanosheets was conducted by chemical reduction of a Pt precursor. An aqueous $[Pt(NH_3)_4]^{2+}$ solution was added to the clay colloid, where the cationic Pt complex was adsorbed on the negatively charged clay layers. Then, the colloid was added by $NaBH_4$ and stirred for 3 h to deposit the Pt particles. The Pt-deposited clay particles were centrifuged and redispersed in water.

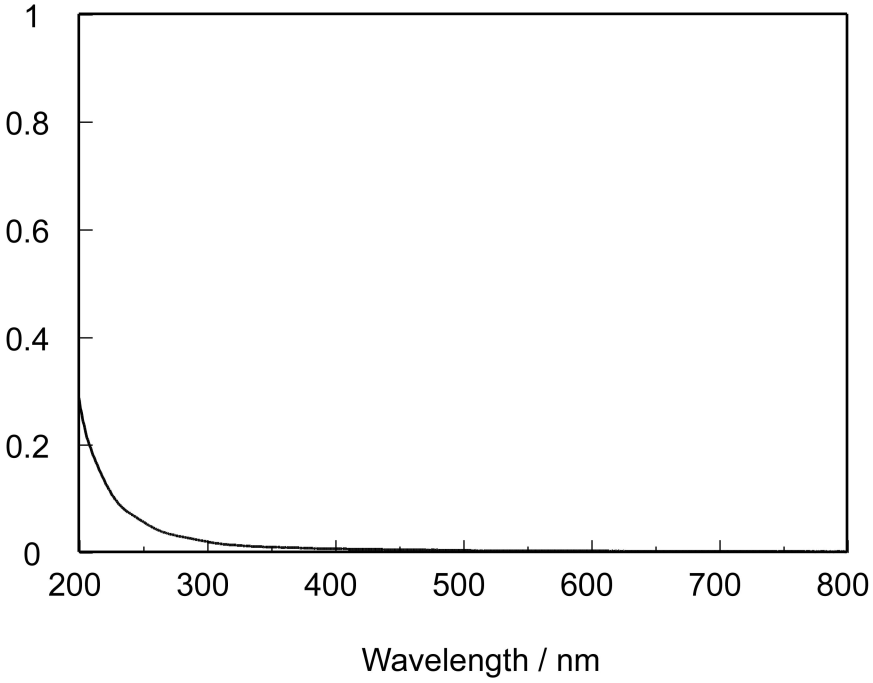
Multicomponent colloids based on the niobate nanosheets were prepared by simple mixing of the niobate colloid (or Pt-loaded niobate colloid) and clay colloid (or Pt-loaded clay colloid). Electrolyte (NaCl or $CaCl_2$) was introduced to the system by dropwise adding its aqueous solution (~ 1 mol L^{-1}). The obtained colloidal mixtures were kept static for a day in the dark prior to the photocatalytic reactions.

(2) Light absorption profile of the samples

UV-visible spectra of the colloidal niobate nanosheets and clay particles are shown below. The spectrum of the niobate nanosheets is in accordance with the diffuse reflectance spectrum reported by the Osterloh's group.[4] The niobate nanosheet colloid exhibits an absorption band due to the band-gap excitation in the UV region but does not have absorption in the visible region. The clay colloid does not exhibit any absorption band in the UV-visible region although light scattering is observed in the UV region.



UV-visible spectrum of the colloid of the niobate nanosheets (0.1 g L^{-1}). The measurement was carried out with a transmission method using a 1-mm length quartz cell.



UV-visible spectrum of the colloid of the clay (Laponite) particles (5 g L^{-1}). The measurement was carried out with a transmission method using a 5-mm length quartz cell.

(3) Photocatalytic hydrogen evolution from water

A multicomponent colloid sample (50 mL) was poured into the 85 mL Pyrex optical cell. A small amount of methanol was added in some cases as the sacrificial electron donor (see Table 1). The cell was capped with a rubber septum, and placed in a water bath equipped with a quartz window. The colloid sample was bubbled with N_2 for 30 min, and subjected to irradiation with the mercury lamp. Details of the UV irradiation are described later. The sample was stirred with a magnetic stirrer at 297 K during the photocatalytic reaction. A small portion of the gas in the headspace of the cell was repeatedly pulled out by a syringe, and analyzed by gas chromatography (Shimadzu GC-14) equipped with a molecular sieve 5A column and a thermal conductivity detector. TiO_2 supplied from the Catalysis Society of Japan as a JRC-TIO-4 reference catalyst (the same as Aerosil P-25) and unexfoliated powdered $K_4Nb_6O_{17}$ were also examined with this method.

(4) UV light irradiation

We employed a Pyrex cylindrical optical cell (i.d. 4.6 cm, length 5 cm, 85 mL) for the UV light irradiation in the Pt photodeposition and photocatalysis experiments. A 50 mL portion of the colloid was introduced into the cell, and the cell was capped with a rubber septum. The cell was then placed in a water bath made of glass equipped with a circular quartz window (ca. 5 cm diameter). The water bath was kept at 297 K by circulating thermostated water. Then, the colloid was irradiated through the quartz window by using a 250 W high-pressure Hg lamp (USHIO USH-250SC) equipped in a lamp house (USHIO SX-UI 251HQ). According to the brochure available on the web site of Ushio Inc. (http://www.ushio.co.jp/), the lamp apparatus generates parallel UV light with the diameter of 5 cm and UV intensity of 42 mW cm^{-2}. We did not use optical filters.

(5) Characterizations

Transmission electron microscope (TEM) observations were carried out with a Hitachi H-7100 microscope operating at 100 kV. A colloid sample was loaded on a grid coated with collodion membrane, dried under ambient conditions, and subjected to the observations. The niobate nanosheets' lateral size was estimated by measuring more than 100 edge lengths of the nanosheets observed by TEM. XRD diffractograms were recorded on a Rigaku Ultima IV diffractometer (monochromated Cu Kα radiation).

References

1. N. Miyamoto and T. Nakato, *J. Phys. Chem. B*, 2004, **108**, 6152-6159.
2. K. Nassau, J. W. Shiever and J. L. Bernstein, *J. Electrochem. Soc.*, 1969, **116**, 348-353.
3. T. Nakato, N. Miyamoto, A. Harada and H. Ushiki, *Langmuir*, 2003, **19**, 3157-3163.
4. M. C. Sarahan, E. C. Carroll, M. Allen, D. S. Larsen, N. D. Browning and F. E. Osterloh, *J. Solid State Chem.*, 2008, **181**, 1678-1683.

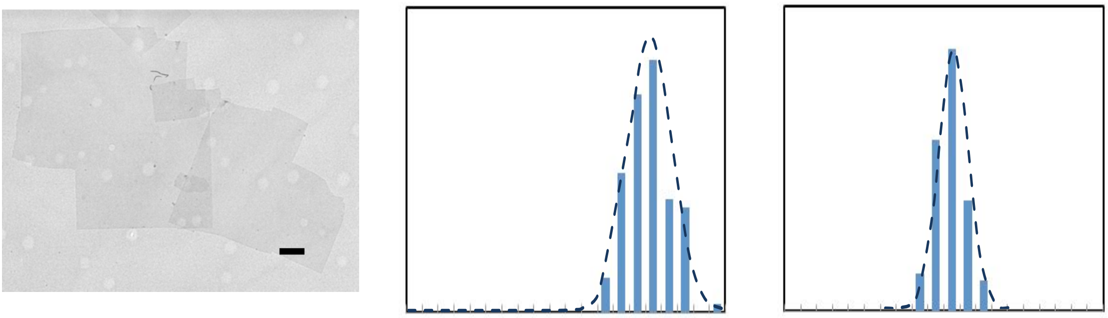
Table S1

Table S1. Composition of the examined multicomponent photocatalytic systems based on the niobate nanosheets.

System	Entry[a]	Composition				
		Niobate	Clay	NaCl	Pt	CH_3OH
		g L^{-1}	g L^{-1}	mmol L^{-1}	wt%	vol%
Niobate	1	1	—	—	—	—
TiO_2	2	1[b]	—	—	—	10
Niobate	3	1	—	—	—	10
Niobate/Pt-loaded clay/NaCl	4	1	10	100	1	—
Niobate/Pt-loaded clay	5	1	10	—	1	—
Pt-loaded niobate	6	1	—	—	1	—
Pt-loaded niobate/clay/NaCl	7	1	10	100	1	—
Niobate/clay	8	1	10	—	—	—
Niobate/NaCl	9	1	—	100	—	—
Niobate/clay/NaCl	10	1	10	100	—	—
Pt-loaded niobate/clay	11	1	10	—	1	—
Pt-loaded niobate/NaCl	12	1	—	100	1	—
Niobate/Pt-loaded clay/NaCl	13	1	10	6	1	—
Niobate/Pt-loaded clay/NaCl	14	1	10	20	1	—
Niobate/Pt-loaded clay/NaCl	15	1	10	40	1	—
Niobate/Pt-loaded clay/NaCl	16	1	10	180	1	—
Niobate/Pt-loaded clay/NaCl	17	1	10	300	1	—
Niobate/Pt-loaded clay/$CaCl_2$	18	1	10	100[c]	1	—

[a] Corresponding to the entry in Figure 1.
[b] Concentration of TiO_2.
[c] Concentration of $CaCl_2$.

Figure S1

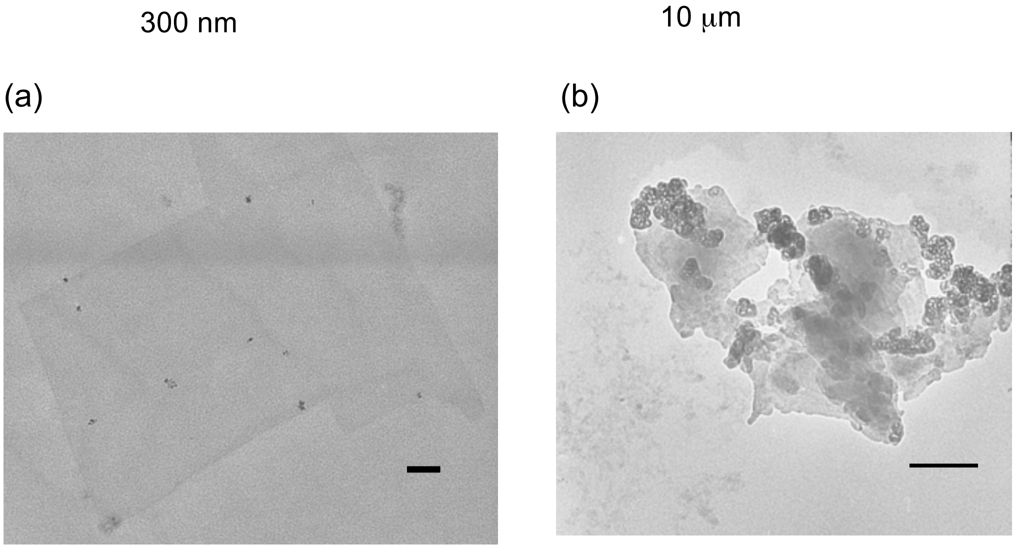


(a) Typical TEM image of the niobate nanosheets.

(b) Lateral size distribution estimated from TEM images for the niobate nanosheets used for the photocatalytic reactions other than entries 2 and 4.

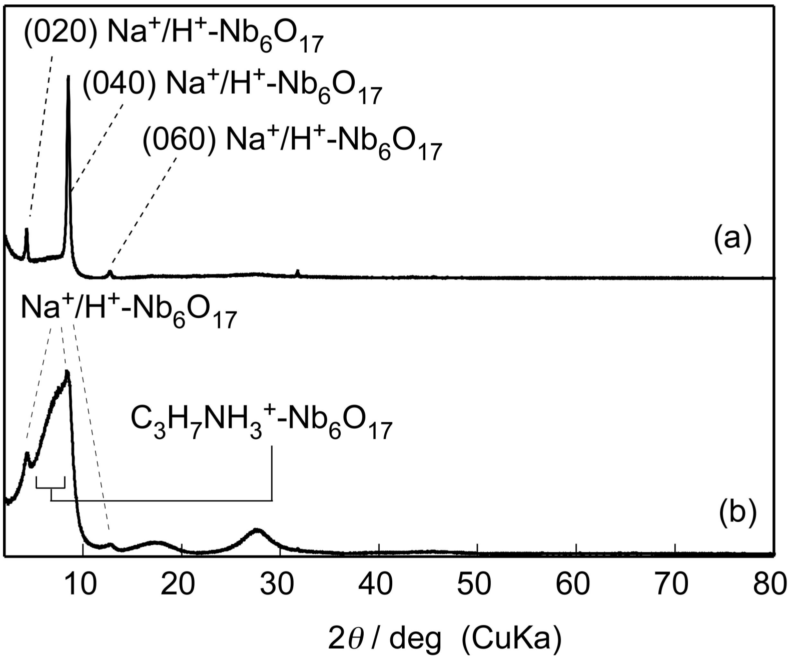
(c) Lateral size distribution estimated from TEM images for the niobate nanosheets used for the photocatalytic reaction of entry 4.

Figure S2



Typical TEM images of (a) Pt-loaded niobate nanosheets and (b) Pt-loaded clay particles.

Figure S3



XRD patterns of the solid components recovered by drop casting from the multicomponent photocatalytic systems based on the niobate nanosheets.

(a) Niobate/Pt-loaded clay/NaCl system (corresponding to entry 5).

(b) Niobate/Pt-loaded clay system (corresponding to entry 6).