

## Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub>의 합성 : Oxynitride계 신규 가시광 광촉매

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## The Synthesis of Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> : A New Visible Light Oxynitride Photocatalyst

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### ABSTRACT

신규 Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> 광촉매를 고상합성법처리(solid state synthesis) 후 암모니아가스(NH<sub>3</sub>)에 의한 기상처리법(ammonolysis)으로 합성하였다. 합성된 신규 광촉매 및 이를 다시 Pt 및 RuO<sub>2</sub>를 도핑 하여 H<sub>2</sub>S를 광분해하여 수소를 발생 실험을 수행하였다. 이 신규 oxynitrid계 광촉매는 가시광 하에서 H<sub>2</sub>S를 광분해하여 수소를 발생하는(Quantum yield = 13.5 %) 우수한 광촉매 활성을 보여 주었다.

**주요기술용어** : Photocatalyst(광촉매), Hydrogen(수소), Metal oxide(금속산화물), Photo-decomposition(광분해), Hydrogen sulfide(황화수소)

### 1. Introduction

Among various method of solar energy conversion, much attention has been paid to photocatalytic decomposition of H<sub>2</sub>S splitting for its potential significance in obtaining directly

clean and high energy containing H<sub>2</sub> from abundant H<sub>2</sub>S. Every year, millions tons of H<sub>2</sub>S are produced in the world with natural gas or from refinery plants, it will not remain constant but it expected to increase in the future. Moreover, hydrogen is highly valued as an energy source and an important chemical feedstock for organic synthesis.

The direct thermal decomposition of H<sub>2</sub>S is

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thermodynamically unfavorable up to 1800 K. Photochemical decomposition is another alternative method for H<sub>2</sub>S splitting, but the efficiency of this method depends on the activity of photocatalyst. If successfully developed with an economic viability, this could be the ultimate technology that could solve both energy and environmental problems altogether in the future.

Therefore, development of an active photocatalyst under visible light region has attained immense importance and has become an imperative topic in photocatalysis research today.

Doping of foreign transition elements into an active existing photocatalysts was studied extensively<sup>1-4)</sup>. Especially, Ni and Cu-doped ZnS photocatalysts show activity for H<sub>2</sub> evolution under visible-light irradiation even without Pt catalyst. Many researchers have reported the doping method for CdS, ZnS, VS, VS<sub>4</sub>, WO<sub>3</sub><sup>5-8)</sup>. The nitrides (Ta<sub>3</sub>N<sub>5</sub>), oxynitrides (TaON, LaTiO<sub>2</sub>N) and oxysulfides (Sm<sub>2</sub>Ti<sub>2</sub>S<sub>2</sub>O<sub>5</sub>) have been reported as active photocatalysts<sup>9-13)</sup>.

Another popular route to synthesis a visible light photocatalyst is to replace oxygen by N, C, S etc into the large band gap noble metal oxide anionic network. Domen et al showed that TaON system energy gap could be tuned by adjusting the amount of nitrogen<sup>14)</sup> and therefore, the electrical properties of the material can be modified.

In this paper, we report the synthesis of niobium zirconium oxynitride (Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub>) from Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub> by ammonolysis method. The as-synthesized material in its pristine state was found to be an excellent photocatalyst for the decomposition of H<sub>2</sub>S to hydrogen.

## 2. Experimental Procedure

### 2.1 Synthesis Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub> by solid-state reaction (SSR) route

All samples in this study were prepared from reagent-grade oxides: ZrO<sub>2</sub> (99.9 %, Aldrich, USA) and Nb<sub>2</sub>O<sub>5</sub> (99 %, Strem Chemicals, USA). Appropriate amounts of raw materials for stoichiometric (Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub>) were mixed and ground well then taken in alumina crucible to calcined at 1573 K for 24 h. After cooling to room temperature the calcined product was ground, washed with distilled water then it was dried at 373 K referred as Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub>.

### 2.2. Syntheses of Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> by thermal ammonolysis route

Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> was prepared by heating Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub> as synthesized from the above procedure in a quartz tube reactor under a flow of ammonia gas (flow rate: 20<sup>-100</sup> cm<sup>3</sup>min<sup>-1</sup>) at 1073 K for 2 h. After the reaction times, the heating furnace was switched off and the product powders were allowed to cool to room temperature under pure argon atmosphere, The rose red color powder was obtained is referred as Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub>.

### 2.3 Pt and RuO<sub>2</sub> doping

Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> catalyst was doped with 1 wt% of Pt and RuO<sub>2</sub> using H<sub>2</sub>PtCl<sub>6</sub> and RuCl<sub>3</sub> respectively. Thus, the catalyst was dispersed in water (methanol for Pt) and an appropriate quantity of dopant was added and the resultant suspension was sonicated for 30 min. The solvent was removed on a rotary evaporator and finally oxidized in air for 3 h at 673 K for Pt while for RuO<sub>2</sub> at 973 K. The Pt doped oxidized materials were reduced by H<sub>2</sub> (20 ml/min flow rate) for 2 h at 773 K and reoxidized at 473 K for 1 h. While RuO<sub>2</sub> doped oxidized materials were used as such.

## 2.4 Characterization

Powder X-ray Diffractograms were recorded on a Model Rigaku-D/MaX-2200 V X-ray Diffractometer with CuK radiation with Ni filter. The surface morphology and particle size were determined using a Field Emission Scanning Electron Microscope (FESEM Model JEOL-JSM 6700 F). Transmission Electron Microscopy (TEM) was performed using FE Tecani G<sub>2</sub> (200 KeV). X-ray photoelectron (XPS) spectra were recorded from the prepared samples with ESCA-LABMK-II-LTD analyzer under a vacuum better than  $1 \times 10^{-8}$  Torr, using MgK $\alpha$  radiation and a constant pass energy of 50 eV. The DRS of the as-synthesized photocatalysts was measured by using UV-visible spectrophotometer (Model SHIMADZU UV-2450 at diffuse reflectance mode). The baseline correction was done using calibrated sample of BaSO<sub>4</sub> between 200 to 800 nm.

## 2.5 Measurements of photocatalytic activity

Cylindrical Pyrex photochemical reactor with a quartz window and thermostat water jacket was used for the photocatalytic measurements. A Xe-lamp light source (Oriel) of intensity 450 W with cut-off filter ( $> 420$  nm) was used for the undoped and doped samples. Each experiment was conducted by using 0.5 g of catalyst in 250 ml of KOH solution (0.5 M) with H<sub>2</sub>S flow, 2.5 ml/min. The vigorously stirred suspension was purged with argon for 1 h followed by bubbling of hydrogen sulfide (H<sub>2</sub>S) for about 1 h at room temperature. The excess hydrogen sulfide was trapped in NaOH solution. The amount of evolved hydrogen was measured using graduated gas burette and gas chromatograph (Model Shimadzu GC-14 B, MS-5 Å column, TCD, Ar gas carrier).

The apparent quantum yield<sup>15)</sup> was measured using a 450 W Xe lamp (Oriel) attached with an IR filter (Oriel), an interference filter ( $430 \pm 5$  nm Oriel) and a cutoff filter ( $> 420$  nm; Oriel). The number of incident photons were measured using a silicon photodiode with integrating sphere (Oriel). The quantum yield (%) is calculated by the following equation.

$$\bullet \text{ Quantum yield (\%)} = \frac{\text{[No. of H}_2\text{ molecules evolved} \times 2]}{\text{[No. of incident photons]}} \times 100$$

## 3. Results and Discussion

### 3.1 XRD Analysis

Powder XRD patterns of Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub> and Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> samples are as shown in Fig. 1 The XRD patterns (Fig. 1 (a)) of Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub> showed all the peaks (d-values) are well matching with the reported data of orthorhombic Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub> (JCPDS card No. 72-1745), indicates the reaction was completed for to the proposed stoichiometry of precursors at desired conditions. The oxynitride samples (Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub>) (Fig. 1 (b)) showed similar XRD patterns (orthorhombic Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub>) with little shifting of  $2\theta$  values of each XRD peaks demonstrate that nitrogen might be doped in the material. Therefore, the oxynitride material may have the molecular formula Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub>. The detail crystal structure of these as-synthesized materials is also under investigation.

### 3.2 Electronic band structure by DRS

Ultraviolet-visible diffuse reflectance spectra (UV-DRS) of Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub> and Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> as synthesized materials areas shown in Fig. 2. The

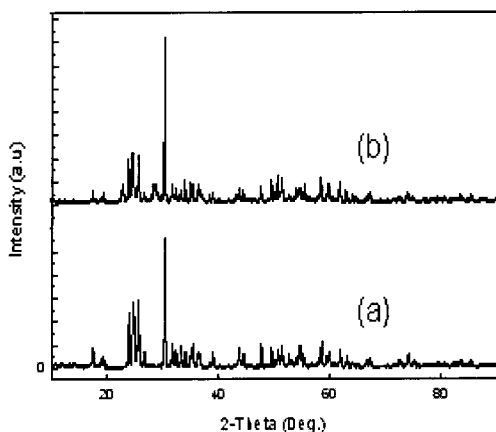


Fig. 1 XRD patterns of (a)  $\text{Nb}_2\text{Zr}_6\text{O}_{17}$  and (b)  $\text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x$  as synthesized samples

nature of absorption band of  $\text{Nb}_2\text{Zr}_6\text{O}_{17}$  suggests that samples are homogeneous with pure phase indicating the completion of the reaction for the proposed stoichiometry but the absorption edge = 400 nm ( $\sim 3.1$  eV) is not in visible range (Fig. 2 (a)).

While the ammonolysis oxynitride sample showed a red shift (Fig. 2 (b)) as compared to its mother material (Fig. 2 (a)). The absorption cut of the  $\text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x$  showed the absorption invisible region at 580 nm (2.14 eV) (which is the major source of solar energy) indicates the nitrogen doped in the oxide samples.

### 3.3 Particle morphology of $\text{Nb}_2\text{Zr}_6\text{O}_{17}$ and $\text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x$ by SEM

Fig. 3 represents Field Emission Scanning Electron Microscopy (FESEM) images of  $\text{Nb}_2\text{Zr}_6\text{O}_{17}$  and  $\text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x$ . The FESEM pictures of  $\text{Nb}_2\text{Zr}_6\text{O}_{17}$  (Fig. 3 (a)) showed agglomeration of uneven elongated orthorhombic particles. While the  $\text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x$  (Fig. 3 (b)) yielded prismatic pseudo orthorhombic shaped particles with some agglomerates and also less

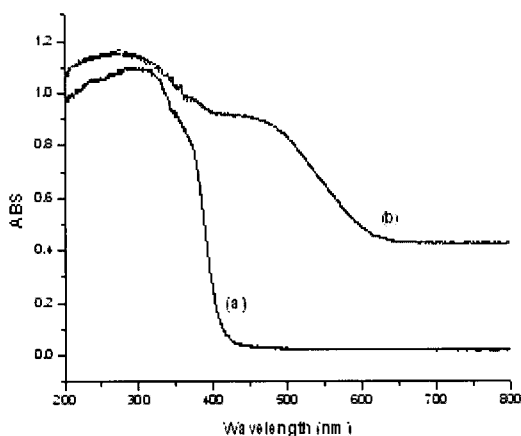


Fig. 2 DRS of (a)  $\text{Nb}_2\text{Zr}_6\text{O}_{17}$  and (b)  $\text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x$  as synthesized samples

denser indicates more porous as compared to its mother material. These agglomerates were found despite the samples were sonicated prior to SEM analysis indicating strong Van der Waal's attraction between the nanoparticles.

Three batches of the same material showed the reproducible shape and size, but with little randomization of homogeneous shapes. SEM photographs have been taken from randomly selected areas of the substrate and as such these are representative of the overall sizes.

### 3.4 Particle morphology of $\text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x$ by TEM

The structural morphology of as-synthesized  $\text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x$  catalyst has been carried out with TEM and selected-area electron diffraction (SAED).

Fig. 4 (a) shows a low-magnification TEM image of  $\text{Nb}_2\text{Zr}_6\text{O}_{17-x}\text{N}_x$  sample showed prismatic pseudo orthorhombic shaped particles clear edges with an average particle size of  $100 \pm 15$  nm which was also observed in SEM results. This indicates the only a few nitrogen atoms was

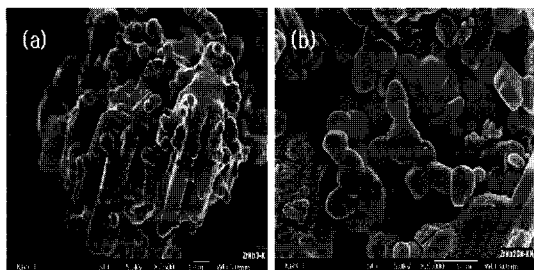


Fig. 3 SEM micrographs of (a) Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17</sub> and (b) Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> as synthesized catalysts

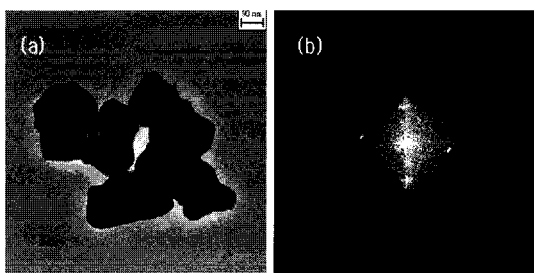


Fig. 4 TEM micrographs of (a) and SAED pattern of Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> as synthesized catalyst

replaced with some of the oxygen of the mother materials oxide hence the geometry and shape are retained in the oxynitride samples. The SAED pattern taken from the same crystalline particle is shown in Fig. 4 (b), which showed the agglomerated crystalline behavior and also the calculated d-values from the pattern are well matched with the XRD results.

### 3.5 Elemental analysis By XPS

Fig. 5 shows the survey by XPS spectra of as-prepared oxynitride (Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub>) sample powder. XPS measurements showed the incorporation of nitrogen into the sample as elemental signal. The binding energies obtained in the XPS analysis are corrected according to the standard value of C 1s. No peaks of other elements except C, O, N, Nb, and Zr are observed on the wide-scan XPS picture, indicating the high

purity of the product. The peak area of these high-resolution scans was measured and is used for calculation of ratio between O and N in the product. The quantification of the peaks shows that atomic ratio of the O : N is 19.66 : 1 indicates the doping of nitrogen in the sample. Since the compound has showed the absorption in the visible region (Fig. 2 (b)) hence further the photocatalytic study of sample powder was carried out to decomposition of H<sub>2</sub>S.

### 3.6 Photocatalytic activities of Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> catalysts

Photocatalytic activity of Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> was investigated for the decomposition of hydrogen sulphide to generate hydrogen under visible light irradiation. Oxynitride samples were doped with Pt and RuO<sub>2</sub> and their photocatalytic activity was

also studied under the identical reaction conditions and the data is summarized in Table 1. The undoped catalyst has shown excellent photocatalytic activity than the doped catalyst. However, the presence of Pt and RuO<sub>2</sub> had little or opposite effect, the one of the reason for

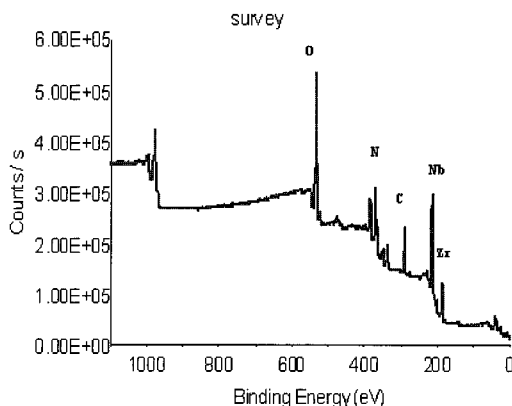


Fig. 5 Elemental survey of Nb<sub>2</sub>Zr<sub>6</sub>O<sub>17-x</sub>N<sub>x</sub> by XPS-analysis

Table 1 Photocatalytic activities of  $Nb_2Zr_6O_{17-x}N_x$  photocatalyst for  $H_2$  evolution from  $H_2S^a$ 

Catalyst	Band gap energy (eV)	$H_2$ evolution rate ( $\mu$ mol/h)	Quantum yield (%)
$Nb_2Zr_6O_{17-x}N_x$	2.14	4283	13.5
$Nb_2Zr_6O_{17-x}N_x^b$	2.14	3446	10.8
$Nb_2Zr_6O_{17-x}N_x^c$	2.14	2766	8.7

The photochemical reaction for the photodecomposition of Catalyst, 0.5<sup>a</sup> g 250 mL (0.5 M aqu.KOH);  $H_2S$  (2.5 mL/min) 450 W Xe lamp (Oriell) with cut-off filter (> 420 nm), <sup>b</sup> Pt and <sup>c</sup>RuO<sub>2</sub> doping

decreased activity maybe due to nitrogen leaching during the thermal treatment of doping process. The rate of evolution hydrogen to undoped and doped with Ni and RuO<sub>2</sub> photocatalyst was found to be stable.

This behavior can be attributed to the non-deposition of sulfur on the surface of the photocatalyst due to the alkaline medium. It is known in the literature that in an alkaline medium sulfide forms soluble disulfide ions hence no sulfur precipitation occurred during the photocatalytic process.  $H_2S$  is followed as per the mechanism reported in our earlier communication<sup>(16)</sup>. The undoped catalyst powders gave 13.5 % quantum yield (the number of photons utilized for a desired chemical reaction divided by the number of photons absorbed by the catalyst) for the  $H_2$  evolution at 550 nm, which is highest among all the photocatalyst reported in the present study. From the result it showed that  $Nb_2Zr_6O_{17-x}N_x$  is an efficient self-deposited photocatalyst to the decomposition of hydrogen sulphide to hydrogen.

#### 4. Conclusions

Thermal ammonolysis of  $Nb_2Zr_6O_{17}N$  at 1073 K gave a new Niobium Zirconium oxynitride

visible light photocatalysts. The undoped photocatalyst showed high activity in the decomposition of hydrogen sulfide to the evolution of hydrogen as compared to the Pt and RuO<sub>2</sub> doped. These are our preliminary results and further modifications in the structure of the photoactive materials are in progress to improve the photocatalytic activity for the decomposition of water and  $H_2S$  for hydrogen production.

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#### References

- 1) Andrew Mills, and Stephen Le Hunte, "A overview of semiconductor particles", J. Photochem. Photobiol. A: Chemistry, Vol. 108, 1997, p. 1.
- 2) H. Kato, and A. Kudo, "Visible-light response and photocatalytic activity of TiO<sub>2</sub> and SrTiO<sub>3</sub> photocatalyst codoped with antimony and chromium", J. Phys. Chem B. Vol. 106, 2002, p. 5029.
- 3) T. Ishii, H. Kudo, and A. Kudo, " $H_2$  evolution from aqueous methanol solution on SrTiO<sub>3</sub> photocatalyst codoped with tantalum and chromium ions under visible light irradiation", J. Photochem. Photobiol. A. Vol. 103, 2004, p. 181.
- 4) T. Ishii, H. Kato, H. Kobayashi, and A. Kudo, " $H_2$  evolution from aqueous methanol solution on SrTiO<sub>3</sub> photocatalyst codoped with tantalum and chromium ions under visible light irradiation", J. Photochem. Photobiol. A. Vol. 163, 2004, p. 181.
- 5) S. A. Naman, "Photoproduction of hydrogen

- sulfide in vanadium sulfide colloidal suspension : effect of temp and pressure", *Int. J. Hydrogen Energy*, Vol. 22, 1997, p. 783.
- 6) D. Park, and J. O. Baeg; "ZnS Photocatalyst, preparation thereof and method for producing hydrogen by use of the same", U.S. Patent No. 6,297,190 B1 (Oct. 2, 2001).
  - 7) D. Park, and J. O. Baeg; "CdZnMs photocatalyst including cations for water decomposition and preparation thereof and method of producing hydrogen by use of the same", U.S. Patent No. 6,517,806 B1 (Feb. 11, 2003).
  - 8) H. Chang, K. Kong, Y. Choi, E. In, Y. Choi, J. O. Baeg, and S. Moon, "Electronic structure of InTaO<sub>4</sub>: A promising photocatalyst", *Chem. Phys. Lett.*, Vol. 398, 2004, p. 449.
  - 9) A. Kudo, K. Omori, and H. Kato, "A novel aqueous process for preparation of controlled crystal formation and highly crystal line BiVO<sub>4</sub> powder from layered vanadates at room temperature and its photocatalytic and photophysical properties", *J. Am. Chem. Soc.*, Vol. 121, 1999, p. 11459.
  - 10) H. Tokunaga, H. Kato, and H. Kudo, "Selective preparation of monoclinic and tetragonal BiVO<sub>4</sub> with sheet like structure and heir photocatalytic properties", *Chem. Mater.*, Vol. 13, 2001, p. 4024.
  - 11) H. Kato, H. Kobayashi, and A. Kudo, "Role of Ag<sup>+</sup> in the band structure and photocatalytic properties of AgMO<sub>3</sub> (M : Ta, Nb) with pyroovskite structure", *J. Phys. Chem.*, Vol. 106, 2002, p. 12441.
  - 12) A. Ishikawa, T. Takata, J. Kondo, M. Hara, K. Kobayashi, and K. Domen, "Oxysulfide<sub>2</sub> Ti<sub>2</sub>S<sub>2</sub>O<sub>5</sub> as a stable photocatalyst for water oxidation and reduction under visible light (650 nm)", *J. Am. Chem. Soc.* Vol. 124, 2002, p. 13547.
  - 13) A. Kasahara, Nukumizu, T. Takata, J. Kondo, M. Hara, H. Kobayash, and K. Domen, "LaTiO<sub>2</sub>N as a visible light(600 nm) driven photocatalyst(2)", *J. Phys. Chem. B*, Vol. 107, 2003, p. 791.
  - 14) M. Hara, T. Takata, J. N. Kondo, and K. Domen, "Photocatalytic reduction of water by TaON under visible light irradiation", *Catalysis Today*, Vol. 90, 2004, p. 313.
  - 15) I. Tsuji, H. Kato and A. Kudo, "Visible-light-induced H<sub>2</sub> evolution from an aqueous solution containing sulfide and sulfite over a ZnS-CuInS<sub>2</sub>-AgInS<sub>2</sub> solid solution photocatalyst", *Angew. Chem., Int. Ed.*, Vol. 44, 2005, p. 3565.
  - 16) B. B. Kale, Jin-Ook Baeg, Jin S. Yoo, Sang Mi Lee, Chul Wee Lee, Sang-Jin Moon, and Hyunju Chang, "Synthesis of a novel photocatalyst, ZnBiVO<sub>4</sub>, for the photodecomposition of H<sub>2</sub>S", *Can. J. Chem.*, Vol. 83, 2005, p. 527.