

Nb-Doped AgTaO<sub>3</sub> as a Water-Splitting Photocatalyst under Visible LightHiroshi Irie<sup>1,2)</sup>, Lei Ni<sup>1)</sup><sup>1)</sup>Clean Energy Research Center, University of Yamanashi 4-3-11 Takeda, Kofu, Yamanashi 400-8511, Japan<sup>2)</sup>Japan Science and Technology Agency, CREST, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

## INTRODUCTION

Since the first report of photo-induced water splitting by TiO<sub>2</sub> electrodes was published (1), the potential of this reaction to convert photon energy into H<sub>2</sub> energy using photoelectrodes and powdered photocatalysts has been extensively investigated. Due to its simplicity, water splitting using a powdered photocatalyst is currently a subject of much interest, with most research focusing on the visible light sensitization of catalysts in order to effectively utilize incoming solar energy. However, the number of visible-light-sensitive photocatalysts that are able to split water into H<sub>2</sub> and O<sub>2</sub> in stoichiometric amounts (overall water splitting) is limited. Domen et al. have reported overall water splitting in the presence of GaN-ZnO photocatalyst under visible-light irradiation (one-step photoexcitation) (2). In contrast, numerous photocatalysts have been identified that can generate either H<sub>2</sub> or O<sub>2</sub> in the presence of sacrificial agents irradiated with visible light (half water splitting), including WO<sub>3</sub>, BiVO<sub>4</sub>, AgNbO<sub>3</sub>, Cr, Ta-co-doped SrTiO<sub>3</sub> (SrTiO<sub>3</sub>:Cr,Ta), Rh-doped SrTiO<sub>3</sub> (SrTiO<sub>3</sub>:Rh), Sm<sub>2</sub>Ti<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, Ta<sub>3</sub>N<sub>5</sub>, and TaON (3). Combined systems with these photocatalysts, such as Pt-deposited SrTiO<sub>3</sub>:Cr,Ta, SrTiO<sub>3</sub>:Rh or Pt-deposited TaON serving as H<sub>2</sub> production photocatalysts, and bare WO<sub>3</sub>, Pt-deposited WO<sub>3</sub>, or BiVO<sub>4</sub> as O<sub>2</sub> production photocatalysts, can become visible-light sensitive photocatalysts for overall water splitting in the presence of a suitable redox couple (4). Such two-step photoexcitation systems are termed “Z-scheme” systems.

With respect to one-step photoexcitation systems, we tried to control the conduction band (CB) of AgTaO<sub>3</sub> by introducing Nb at Ta site to be sensitive to visible light because AgTaO<sub>3</sub> is known to absorb only UV light (5). Then, we achieved the simultaneous evolutions of H<sub>2</sub> and O<sub>2</sub> in the presence of Nb-doped AgTaO<sub>3</sub> irradiated with only visible light.

## EXPERIMENTALS

AgTaO<sub>3</sub>, Nb-doped AgTaO<sub>3</sub> (AgTa<sub>0.7</sub>Nb<sub>0.3</sub>O<sub>3</sub>, AgTaNbO<sub>3</sub>) and AgNbO<sub>3</sub> powders were prepared hydrothermally at 180°C for 48 h with AgNO<sub>3</sub>, Ta(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub> and Nb(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub> as starting materials. The graft of NiO (0.5 wt%) as a co-catalyst onto AgTaNbO<sub>3</sub> was performed by mixing Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O with photocatalysts, followed by calcination 300°C for 1 h. The crystal structures of the prepared photocatalysts (prior to NiO graft) were identified by X-ray diffraction. UV-visible absorption spectra were obtained by the diffuse reflection method.

NiO-grafted AgTaNbO<sub>3</sub> powder was suspended in water. An Xe lamp with an optical filter (Y-44) was employed for light irradiation (> 420 nm). The amounts of evolved H<sub>2</sub> and O<sub>2</sub> were monitored using a gas chromatograph.

## RESULTS AND DISCUSSIONS

AgTaNbO<sub>3</sub> was confirmed to have an almost single phase of AgTaO<sub>3</sub>. Figure 1a shows UV-visible absorption spectra of AgTaO<sub>3</sub>, AgTaNbO<sub>3</sub> and AgNbO<sub>3</sub>. It is obvious from Figure 1a that doping Nb at the Ta site

narrowed the band gap of AgTaO<sub>3</sub> and that the absorption edges shifted to a longer wavelength region. AgTaO<sub>3</sub> is an indirect gap semiconductor and thus the band-gaps of these photocatalysts can be estimated from the tangent lines in the plots of the square root of the Kubelka-Munk functions against the photon energy, as shown in Figure 1b. The tangent lines, which are extrapolated to  $(h\nu\alpha)^{1/2} = 0$ , indicate the band-gaps of 3.4, 2.9 and 2.8 eV for AgTaO<sub>3</sub>, AgTaNbO<sub>3</sub> and AgNbO<sub>3</sub>, respectively. Thus, AgTaNbO<sub>3</sub> can absorb light in a longer wavelength region up to visible light.

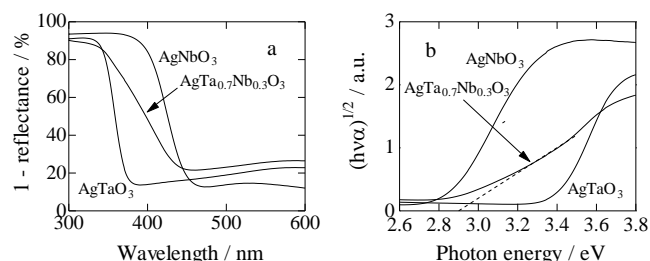


Figure 1. (a) UV-visible absorption spectra of AgTaO<sub>3</sub>, AgTaNbO<sub>3</sub> and AgNbO<sub>3</sub>, (b) plots of the square root of the Kubelka-Munk function against photon energy.

We examined water-splitting over NiO-grafted AgTaNbO<sub>3</sub> under irradiation with visible light (> 420 nm) as shown in Figure 2. The H<sub>2</sub> and O<sub>2</sub> evolved almost linearly with increasing the irradiation time. More importantly, the ratio of evolved H<sub>2</sub> to O<sub>2</sub> was ca. 2 to 1 (stoichiometric amount). Thus, overall water-splitting in the presence of the photocatalyst was achieved.

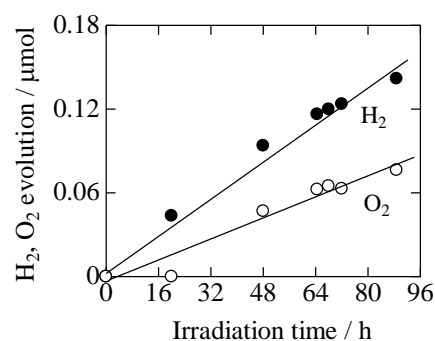


Figure 2. H<sub>2</sub> and O<sub>2</sub> evolutions by water-splitting as a function of time in the presence of the photocatalyst irradiated with visible light.

In summary, we have accomplished the overall water-splitting utilizing NiO-grafted AgTa<sub>0.7</sub>Nb<sub>0.3</sub>O<sub>3</sub> photocatalysts that simultaneously evolve H<sub>2</sub> and O<sub>2</sub> at a molar ratio of ca. 2 to 1 following irradiation with visible-light.

## REFERENCES

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