

New Aspects of Heterogeneous Photocatalysts for Water Decomposition

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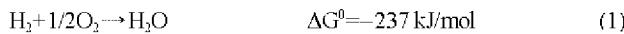
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Abstract—Several new photocatalysts for overall water splitting are described. Under UV light irradiation (270 nm), La-doped NaTaO₃ modified with NiO decomposed water into H₂ and O₂ with extremely high quantum efficiency. Under an optimized condition, the apparent quantum efficiency, which was estimated with numbers of irradiated photons and evolved H₂ molecules, reached 56%. New stable photocatalytic materials containing elements with d¹⁰ electronic configuration such as In³⁺, Sn⁴⁺ and Sb⁵⁺ were developed for overall water splitting. Some mesoporous oxides were proved to be effective photocatalysts. (Oxy)nitrides of some early transition metals, i.e., Ta, Nb and Ti, were found to be stable materials having potentials for H₂ and O₂ evolutions under visible light irradiation (≤ 600 nm). The electronic structures of these photocatalysts are also discussed based on DFT calculation.

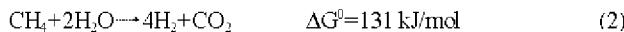
Key words: Photocatalytic Overall Water Splitting, d⁰ and d¹⁰-Metal Oxides, Mesoporous Materials, (Oxy)nitrides, DFT Calculation

INTRODUCTION

In the 21st century, hydrogen is a potential candidate for a clean and high-energy containing energy carrier. H₂ itself is a clean material as the combustion of H₂ produces only pure water with a large amount of heat release.



However, at present H₂ is mainly produced by reforming reactions of hydrocarbon resources such as steam reforming of methane.



In these cases, H₂ production is always accompanied by CO₂ formation and in this meaning such H₂ should not be regarded as a clean energy carrier. From this point of view, the resource of clean hydrogen on the earth is only water due to the reverse reaction of (1).



This reaction is, of course, accompanied by a large amount of energy conversion and the essential importance for this process is to utilize clean and recyclable energies to drive reaction (3). There may be several candidates for them such as hydraulic power, wind force and even nuclear power.

Among them, solar energy is one of the most favorable energy resources because it is essentially clean and recyclable, and it sustains all the lives on the earth. In Table 1, several numbers con-

Table 1. Amount of solar energy

Energy of sun	1.2 $\cdot 10^{34}$ J/y
↓ Outer sphere of the earth	(1/2.2 $\cdot 10^{10}$) 5.5 $\cdot 10^{24}$ J/y
↓ On the sea and land	(1/2 : reflection) 3.0 $\cdot 10^{24}$ J/y
↓ Photosynthesis	(1/1000) 3.0 $\cdot 10^{21}$ J/y
Energy consumption in the world	3.0 $\cdot 10^{20}$ J/y

cerning the solar energy are listed. The sun is steadily emitting a huge energy (1.2 $\cdot 10^{34}$ J/year) and only a small portion of it (1/10¹⁰) is provided on the earth. About a half of the energy (3.0 $\cdot 10^{24}$ J/y) can penetrate the atmosphere onto the sea and land surfaces. This is the energy available for us on the earth. It should be emphasized that photosynthesis reaction in nature fixes 0.1% of the solar energy on the earth. The energy consumption in the world by human beings is about 0.01% of the solar energy (3 $\cdot 10^{20}$ J/y). Another interesting number is that the total amount of the energy accumulated in all fossil resources corresponds to the solar energy of only 7 days. Therefore, the amount of solar energy available on the earth far exceeds that needed to maintain modern civilization. Judging from the numbers cited above, however, if one simply estimates the surface area to be used to fix an enough amount of solar energy, it would be huge. If we had a system with the efficiency of solar energy conversion of 10%, the area would be on the order of 10⁵ km². This means that the method of solar energy conversion has to have applicability to such a wide area.

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Table 2. Water splitting over alkali and alkaline earth tantalate photocatalysts

Catalyst	Band gap/eV	NiO loaded/mass ^{0.0}	Activity/μmol/h	
			H ₂	O ₂
LiTaO ₃	4.7	0.10	98	52
NaTaO ₃	4.0	0.05	2180	1100
KTaO ₃	3.6	0.10	7.4	2.9
CaTa ₂ O ₆	4.0	0.10	72	32
SrTa ₂ O ₆	4.4	0.10	960	490
BaTaO ₆	4.1	0.30	629	303

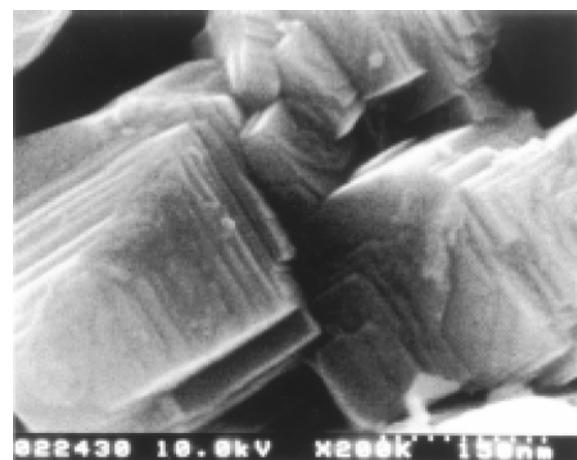
Alkali tantalates were prepared in the presence of excess amounts (50%) of alkali. Photocatalyst: 1.0 g, water: 390 ml, reaction cell: inner irradiation-type reaction cell made of quartz, light source: 400 W high pressure mercury lamp.

Since 1998 the authors have been carrying out a CREST (Core Research for Evolutional Science and Technology) project of JST (Japan Science and Technology Co.). The purpose is to develop highly efficient photocatalytic systems to generate H₂ from water based on inorganic materials. We expect such photocatalysts will have a possibility to be applied in a huge scale. In this paper, several new photocatalysts, which have been developed in this project, are briefly described.

NEW PHOTOCATALYSTS UNDER UV LIGHT IRRADIATION

1. La-doped NiO/NaTaO₃: High Quantum Efficiency

Recently, various tantalates have been examined as photocatalysts for overall water splitting [Kato and Kudo, 1999; Kudo et al., 2000]. Among ATaO₃ (A=Li, Na, K) and BTa₂O₆ (B=Ca, Sr, Ba) modified by NiO, NaTaO₃ showed noticeable activity for stoichiometric H₂ and O₂ evolution (see Table 2). They further examined the effect of doping of lanthanides, and found that La-doped NiO/NaTaO₃ showed extremely high activity of water decomposition under UV light irradiation; the rate of H₂ evolution reached 15-20 mmol/h and the estimated quantum efficiency was 56% (400 W

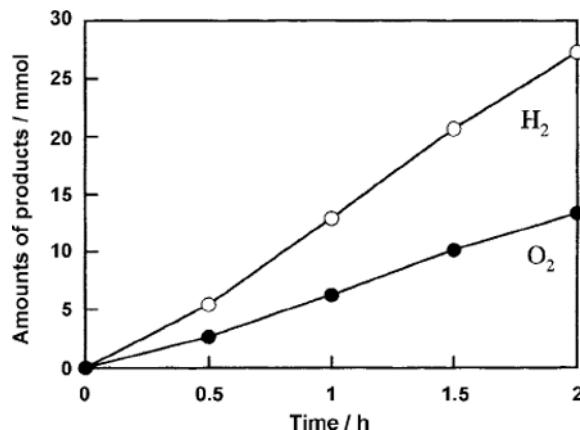
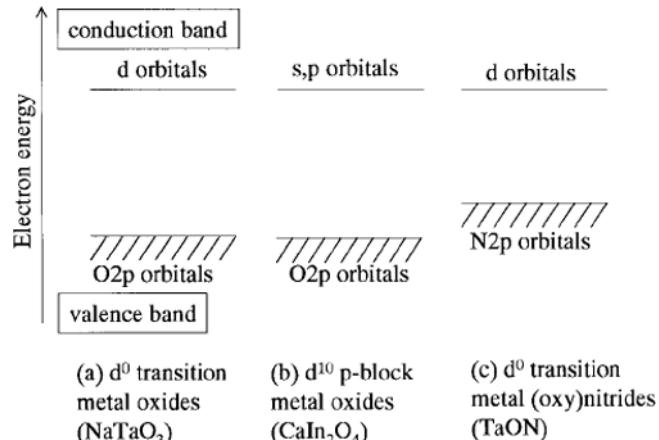
**Fig. 2. SEM image of La (1.5 mol%)-doped NaTaO₃.**

high pressure mercury lamp; inner irradiation type reaction vessel) [Kudo and Kato, 2000]. A typical time course of H₂ and O₂ evolution on NiO (0.2 wt%)/NaTaO₃:La (1.5 mol%) in an aqueous NaOH solution (1 mM) is shown in Fig. 1. Although the time course shown is for 2 h, the activity is stable more than 200 h. They attributed the effect of La doping to the change of morphology of NaTaO₃ particles, i.e., the particle size decreased from 2-3 μm to 0.1-0.7 μm by La doping and a noticeable step structure was formed for La-doped NaTaO₃ as shown in Fig. 2. Obviously, the decrease of the particle size is advantageous for the increase of photocatalytic activity, but the merit of the stepped structure is not so clear at present.

2. Photocatalysts Containing Elements with d¹⁰ Electronic Configuration

So far, most of the photocatalysts developed for the decomposition of water into H₂ and O₂ have been NiO- or RuO₂-loaded titanates, niobates, zirconates and tantalates [Inoue et al., 1991; Domen et al., 1980; Sayama and Arakawa, 1994]. The common feature of these photocatalysts is being composed of octahedrally coordinated d⁴ transition metal ions such as Ti⁴⁺, Zr⁴⁺, Nb⁵⁺ and Ta⁵⁺. It is known that for these photocatalysts the valence band mainly consists of O 2p orbitals and the conduction band empty d orbitals of the transition metal cations [Fig. 3(a)] [Scaife, 1980].

Some d¹⁰ oxides, e.g. ZnO, Cu₂O, In₂O₃ and SnO₂, have been

**Fig. 1. H₂ and O₂ evolution on NiO (0.2 wt%)/NaTaO₃:La (1.5 mol%) in an aqueous NaOH solution (1 mM) under ultraviolet light irradiation.****Fig. 3. Band structures of some photocatalyst groups.**

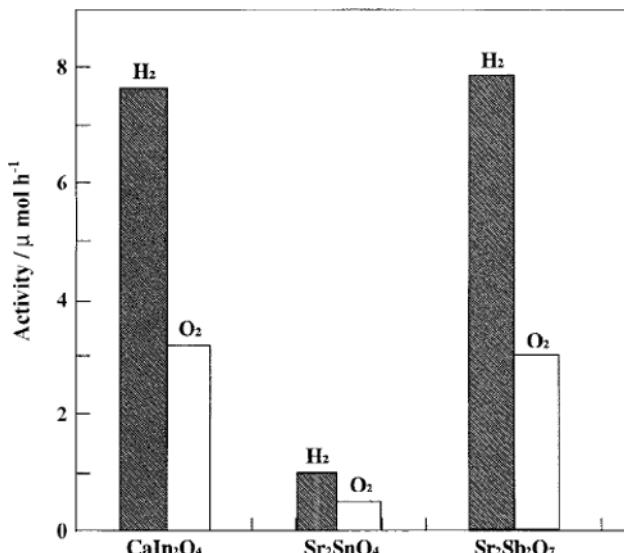


Fig. 4. Photocatalytic activities of some RuO₂-loaded p-block metal oxides.

known as typical semiconductors and show some photocatalytic activities; however, they are not available for overall water splitting because of their unstability and/or unsuitable positions of conduction and valence bands [Scaife, 1980]. Y. Inoue et al. have paid attention to p-block metal oxides with d¹⁰ configuration. As a result, they have found several mixed oxides containing p-block metal cations of d¹⁰ configuration such as CaIn₂O₄, Sr₂SnO₄, Sr₂Sb₂O₇ are stable and active for water decomposition when they are modified by RuO₂ [Sato et al., 2001]. In Fig. 4, rates of H₂ and O₂ evolution on these oxides modified by RuO₂ are shown. In all cases almost stoichiometric evolutions of H₂ and O₂ were confirmed and the activities were stable for more than several tens of hours. Some of these have absorptions in visible light (>400 nm); however, the photoresponses were observed only in UV light region. In Fig. 3(b), the band structure calculated by DFT is shown. The bottom of the conduction band mainly consists of s, p orbitals of metallic elements. These results clearly demonstrate that the choice of materials available for water decomposition is extended significantly, and it is stimulating the idea for the development of new materials being responsive in visible light region.

3. Mesoporous Materials as Photocatalysts

As introduced in a previous section, tantalates are found to be highly active photocatalysts for overall water decomposition under UV irradiation. For the purpose of development of new types of photocatalysts, some mesoporous transition metal oxides have been synthesized [Takahara et al., 2001; Kondo et al., 2001; Lee et al., 2001]. Among them, pure tantalum [Takahara et al., 2001] and magnesium-tantalum mixed oxides showed considerable photoactivity for water splitting, even though the oxide walls consisted of amorphous phases. Mesoporous magnesium-tantalum (Mg-Ta) mixed oxide is prepared from a sol-gel method: MgCl₂ (0.003 mol) and TaCl₅ (0.007 mol) were mixed in ethanol (10 g) containing a Pluronic block copolymer HO(CH₂CH₂O)₁₀(CH₂CH(CH₃)O)₁₀(CH₂CH₂O)₁₀H (1 g, P-123). After aging at 40°C for 7–10 days, the surfactant-containing Mg-Ta mixed oxide was calcined at 500°C for 30 h for the formation of mesopores by removing the block copolymer tem-

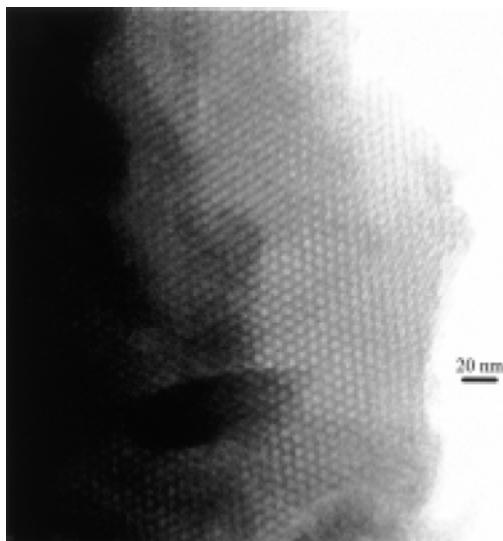


Fig. 5. Transmission electron microscopy (TEM) image of the mesoporous Mg-Ta mixed oxide obtained on a JEOL 2010F electron microscope operated at 200 kV.

plate.

In a TEM image of mesoporous Mg-Ta mixed oxide (Fig. 5), ordered mesopores are clearly observed. BET surface area, pore size and wall thickness of the prepared mesoporous Mg-Ta mixed oxide were found as 123 m²·g⁻¹, 5.0 nm and 3.6 nm, respectively, from analysis of the N₂ adsorption-desorption isotherm together with XRD patterns. The homogeneous mixing of Mg and Ta in 3 : 7 ratio was confirmed by an energy dispersive X-ray (EDS) analysis in c. 5 nm spots of the sample using TEM apparatus. The photocatalytic activity of the mesoporous Mg-Ta mixed oxide (0.3 g) was studied after loading NiO (0.1 wt%) in pure water (420 mL) by UV irradiation (450 W Hg lamp). The results were compared under the

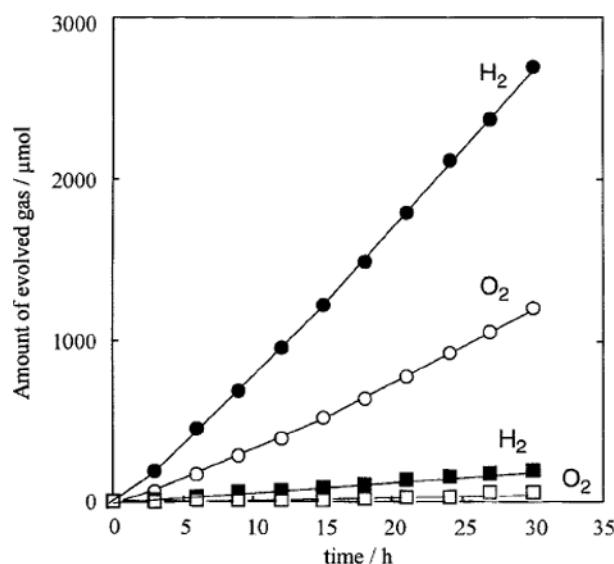


Fig. 6. Comparison of photocatalytic activity of NiO (0.1 wt%) loaded mesoporous Mg-Ta mixed oxide (circle) and Mg-Ta₂O₆ (square) for overall decomposition of water under UV irradiation.

same condition with those of a crystallized MgTa_2O_6 prepared by a solid-state reaction. As shown in Fig. 6, water decomposition into the stoichiometric H_2 and O_2 over the mesoporous Mg-Ta mixed oxide at much higher rate than the MgTa_2O_6 was observed. For photocatalytic reactions, a crystallized lattice structure is preferable due to the better mobility of the excited electrons and positive holes. However, mesoporous Mg-Ta mixed oxide resulted in higher photocatalytic activity for overall water decomposition than the crystallized MgTa_2O_6 . Therefore, mesoporous structure is expected to be advantageous to the photocatalytic reactions possibly due to the short distance of migration of the excited electrons from bulk to the surface, although the wall structure is amorphous.

NEW PHOTOCATALYTIC MATERIALS UNDER VISIBLE LIGHT IRRADIATION: (OXY)NITRIDES AS VISIBLE LIGHT RESPONSIVE PHOTOCATALYSTS

So far, no photocatalyst has effectively worked under visible light irradiation (>400 nm) for overall water splitting. As mentioned above, all the catalysts successfully applied to water decomposition were oxides and absorbed only UV light (<400 nm). The wide band gaps of the oxides are attributed to the deep O 2p levels consisting the top of the valence bands [see Fig. 3(a) and 3(b)]. One of the strategies to reduce the band gap energy maintaining the potential of overall water splitting is to introduce new electron filled orbitals on top of the O 2p valence band.

To examine such a possibility, Domen et al. examined (oxy)nitrides of early transition metals such as Ti, Nb and Ta. According to the DFT calculation of some oxynitrides of tantalum by H. Kobayashi, the bottom of the conduction band mainly originates in Ta 5d orbitals and the top of the valence band consists of hybrid orbitals of N 2p and O 2p orbitals, in which the contribution of N 2p is more significant than that of O 2p [see Fig. 3(c)]. Based on this calculation, it is expected that the electronic energy level of the bottom of the conduction band is maintained as high as that of a corresponding oxide, while the top of the valence band shifts to a higher (or more negative) position than that of oxides, which results in a smaller band gap energy maintaining potentials for overall water

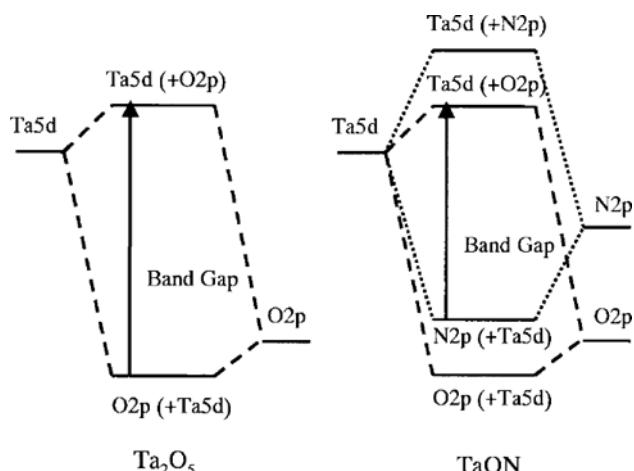


Fig. 7. Comparison of band structures of tantalum oxide and oxy-nitride.

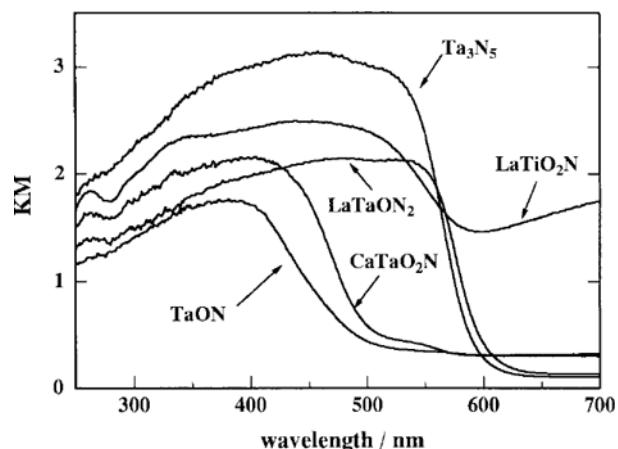


Fig. 8. UV-Vis diffuse reflectance absorption spectra of various (oxy)nitrides.

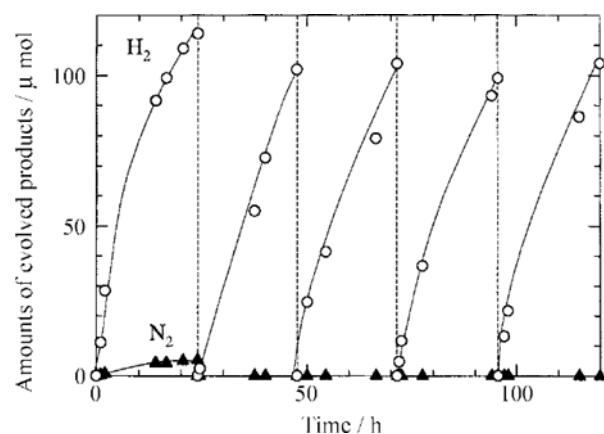


Fig. 9. H_2 evolution on Pt (3.0 wt%)/TaON in aqueous MeOH (10 vol%) solution under visible light irradiation.

splitting (see Fig. 7). Some of the UV-vis diffuse reflectance absorption spectra are shown in Fig. 8. These (oxy)nitrides have absorption edges in the middle of the visible light region, i.e., 500–650 nm. Next, photocatalytic properties of these materials were examined. As test reactions to examine H_2 and O_2 evolution capabilities, H_2 evolution reaction in an aqueous methanol solution and O_2 evolution reaction in an aqueous silver nitrate solution were used, respectively. In the former reaction, 3 wt% of Pt was loaded as a co-catalyst for H_2 evolution. Here, the results of TaON are shown as a typical example of oxynitrides. Fig. 9 is the time course of H_2 evolution reaction under visible light irradiation (>420 nm) in an aqueous methanol solution. H_2 evolved steadily and N_2 evolution, which was the product of the catalyst's degradation through oxidation of N^{3-} anions, was negligible. The apparent quantum efficiency of H_2 evolution was ca. 0.2%. This indicates that the conduction band of TaON has the potential to reduce H^+ into H_2 . On the other hand, O_2 evolution reaction under visible light irradiation (>420 nm) in an aqueous silver nitrate is shown in Fig. 10. The pH of the initial solution was controlled at about 8 by adding La_2O_3 powder. Under this condition, O_2 evolved rapidly in the beginning of the reaction and the rate decreased gradually with the consumption of Ag^+ cations and the decrease of the pH. The initial apparent quantum ef-

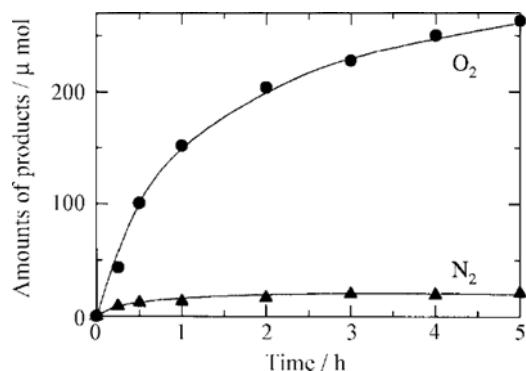


Fig. 10. O₂ evolution on TaON in aqueous AgNO₃ (0.01 M) solution under visible light irradiation.

iciency of the O₂ evolution was ca. 10%. Again N₂ evolution was negligible. From the result, it is concluded that the valence band of TaON has enough potential to oxidize water into O₂. It is also suggested that this oxynitride, TaON, is a stable material during water decomposition. Other (oxy)nitrides such as Ta₃N₅, LaTiO₂N showed similar behaviors for H₂ and O₂ evolution reactions, which indicates these materials also have the potential for overall water splitting. As mentioned above, at present O₂ evolution efficiency (ca. 10%) is high enough while H₂ evolution efficiency (ca. 0.2%) is rather low. We suspect the low efficiency of H₂ evolution is due to the surface states located in the band gap, and for this reason overall water splitting has not been accomplished. Therefore, our major efforts are now being concentrated to improve the property of H₂ evolution.

In any case, to the best of our knowledge, these are the first examples that have the potential to decompose water with reasonable absorption in a visible light region without being accompanied by degradation of the catalysts.

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