Development of Photocatalyst Materials for Water Splitting with the Aim at Photon Energy Conversion

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A photocatalyst which has extensively been studied so far is TiO₂ with a 3.0–3.2 eV band gap. Well-known photocatalysts with visible-light response are only Pt/CdS and WO₃. Thus, photocatalyst materials mainly employed have been so limited. In such a background, new photocatalysts with high activity have recently been developed. Alkali and alkaline earth tantalates have arisen as a new group of photocatalyst materials for water splitting into H₂ and O₂ under ultra-violet light irradiation. They showed the activities even without co-catalysts such as Pt, being different from titanate photocatalysts. When NiO co-catalysts were loaded on tantalate photocatalysts, except for LiTaO₃, the photocatalytic activities were drastically increased. Among the tantalates, NiO/NaTaO₂ showed the highest activity. Moreover, the activity of NiO/NaTaO₂ was improved by La-doping. On the other hand, highly crystalline BiVO₄ powders with scheelite (monoclinic) and zircon type (tetragonal) structure were selectively synthesized by an aqueous process. The BiVO₄ powder with the scheelite structure showed a high photocatalytic activity for O₂ evolution in the presence of sacrificial reagent (Ag⁺) under visible light irradiation (λ > 420 nm). The photocatalytic activity of the BiVO₄ powder prepared by the aqueous process was much higher than that of BiVO₄ prepared by a conventional solid state reaction. Znₐ₋₀·₇Cu₀·₃S (band gap: 2.5 eV) and Znₐ₋₀·₀Ni₀·₁S (band gap: 2.3 eV) photocatalysts showed high activities for H₂ evolution from an aqueous K₂SO₃ and Na₂S solution under visible light irradiation without co-catalysts such as Pt. Zn₂Nb₂O₇, Bi₂W₂O₉, Bi₃WO₉, and Bi₃TiNbO₉ consisting of ions with d¹⁰ and s² configuration were also active for H₂ or O₂ evolution from aqueous solutions containing sacrificial reagents.

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ENERGY and environmental issues in a global level are important themes tackled in the 21st century. It is indispensable to construct clean energy systems in order to solve the issues. Hydrogen will play an important role in the system. At present, hydrogen is mainly produced from fossil fuels such as natural gas by steam reforming. Hydrogen should ideally be produced from water using natural energies such as solar light. The photon energy is converted to chemical energy accompanied with a large positive change in the Gibb's free energy free through water splitting.

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \quad \Delta G^o = -237 \text{kJ/mol} \quad (1)
\]

Therefore, photocatalytic water splitting is regarded as an artificial photosynthesis. In this sense, water splitting by a photocatalyst may be an ultimate reaction to solve the energy and environmental issues. The development of highly functional materials which can harvest solar light energy, separate the photogenerated charge, and cause a redox reaction on the surface is a key point in order to put the artificial photosynthesis with photocatalysts into practice. Since the Honda–Fujishima effect using a TiO₂ electrode was found,²¹²² numerous researchers have extensively studied water splitting using semiconductor photoelectrodes and photocatalysts. However, they had not succeeded to discover efficient materials for water splitting into H₂ and O₂ under visible light irradiation. Accordingly, the photon energy conversion by water splitting using photocatalysts has been considered to be pessimistic, and its research activity has been sluggish to date. At present, applications for self-cleaning and anti-fogging are major commercialization of TiO₂ photocatalysts in our life spaces.¹³ However, new photocatalyst materials for water splitting have recently been discovered one after another and the research in photocatalytic water splitting seems to be advanced.¹⁴,²³ Although the photon energy conversion using photocatalysts is far from practical use at the present stage, the photocatalytic water splitting will be an important project in the long view.

The photocatalysis research has been carried out mainly in fields of electrochemistry, catalyst chemistry, and photochemistry. The research from the view point of material science is also very important because many heterogeneous photocatalysts are ceramic materials of oxides and sulfides. Therefore, it is no doubt that ceramics science will largely contribute to the global energy and environmental issues through the development of photocatalyst materials for water splitting.

In the present paper, photocatalyst materials for water splitting are reviewed. The fundamental aspects of photocatalyst are explained and photocatalysts which have been reported so far are surveyed. After that, new photocatalysts that the author’s group has recently found are introduced.

2. Basis of photocatalytic reactions

Many heterogeneous photocatalysts have semiconducting properties because photocatalytic reactions proceed as schematically shown in Fig. 1. Semiconductors have the band structure in which the conduction band is separated from the valence band by a band gap with a suitable width. When light of which the energy is larger than the band gap is irradiated, electrons and holes are generated in the conduc-
Development of Photocatalyst Materials for Water Splitting with the Aim at Photon Energy Conversion

The photogenerated electrons and holes cause redox reactions similarly to electrolysis. Water molecules are reduced by the electrons to form hydrogen and are oxidized by the holes to form oxygen for overall water splitting as shown in Fig. 1 (a). Important points in the semiconductor photocatalyst materials are a width of the band gap and potentials of the conduction and valence bands. The bottom level of the conduction band has to be more negative than the redox potential of \( \text{H}^+ / \text{H}_2 \) (0 V vs. NHE), while the top level of the valence band be more positive than the redox potential of \( \text{O}_2 / \text{H}_2\text{O} \) (1.23 V). Therefore, the band gap should be larger than 1.23 eV.

Water splitting using photocatalysts would seem to be simple and easy as shown in Fig. 1 (a). However, it is a very tough reaction because of an uphill reaction in which back reactions easily proceed. The potentials for water splitting which the band structure should satisfy are merely thermodynamically necessary conditions but not sufficient. Complicated factors are actually concerned with the photocatalytic properties as shown in Fig. 2. The photocatalytic properties are strongly affected by bulk properties such as crystallinity. The better the crystallinity is, the less the number of defects which often work as recombination sites between photogenerated electrons and holes, resulting in increases in the life time and mobility. On the other hand, the number and quality of the active sites for a redox reaction by photogenerated electron and hole pairs, and the overpotential for the redox reaction are kinetically affected by surface properties. For example, the number of the active site depends on the surface area. Even if the photogenerated electrons and holes possess thermodynamically sufficient potential for water splitting, they will have to recombine with each other if the active sites for a redox reaction do not exist on the surface. Therefore, co-catalysts such as Pt and NiO are often loaded on the surface in order to introduce the active sites. It depends on the photocatalytic reaction which factor is predominant. For example the crystallinity is an important factor rather than the surface area for water splitting in the absence of sacrificial reagents. Thus, suitable bulk and surface properties, and energy structure are necessary for photocatalysts. So, it is understandable that photocatalysts should be highly functional materials.

Sacrificial reagents are often employed to evaluate the photocatalytic activity for water splitting (Figs. 1 (b) and (c)), because overall water splitting is a tough reaction. When the photocatalytic reaction is carried out in aqueous solutions including easily oxidizable reducing reagents such as alcohol and EDTA, photogenerated holes irreversibly oxidize the reducing reagents instead of water. It makes the electrons in the photocatalyst rich and a \( \text{H}_2 \) evolution reaction is enhanced as shown in Fig. 1 (b). On the other hand, in the presence of electron acceptors such as \( \text{Ag}^+ \) and \( \text{Fe}^{3+} \), the photogenerated electrons in the conduction band are consumed by them and an \( \text{O}_2 \) evolution reaction is enhanced as shown in Fig. 1 (c). However, these reactions using sacrificial reagents are just the test reactions to evaluate if a certain photocatalyst satisfies the thermodynamic and kinetic potentials for \( \text{H}_2 \) and \( \text{O}_2 \) evolution. The results do not guarantee a photocatalyst to be active for overall water splitting into \( \text{H}_2 \) and \( \text{O}_2 \) in the absence of sacrificial reagents.

3. General view of photocatalyst materials for water splitting

Photocatalysts which produce \( \text{H}_2 \) and \( \text{O}_2 \) in stoichiometric amounts with reasonable activities are listed in Table 1. \( \text{TiO}_2 \) has extensively been studied for a long time. At the initial stage of the research, it was questionable that a platinized \( \text{TiO}_2 \) photocatalyst could decompose water because the activity was usually low and no \( \text{O}_2 \) evolution was often observed. After that, NaOH-coating and an addition of alkali carbonates have been found to be effective for water splitting on the Pt/TiO\(_2\) photocatalyst.\(^6\),\(^8\) Moreover, it was recently clarified that the Pt/TiO\(_2\) photocatalyst can decompose pure water by irradiating light from upper side of a reaction cell to prevent the back reaction between evolved \( \text{H}_2 \) and \( \text{O}_2 \) on the Pt co-catalyst.\(^9\) \( \text{SrTiO}_3 \) with the perovskite structure has also been used as a photocatalyst. Domen and co-workers have reported that \( \text{NiO} \)-loaded \( \text{SrTiO}_3 \) powder can decompose pure water by irradiating light from upper side of a reaction cell to prevent the back reaction between evolved \( \text{H}_2 \) and \( \text{O}_2 \) on the Pt co-catalyst.\(^9\) \( \text{SrTiO}_3 \) with the perovskite structure has also been used as a photocatalyst. Domen and co-workers have reported that \( \text{NiO} \)-loaded \( \text{SrTiO}_3 \) powder can decompose pure water into \( \text{H}_2 \) and \( \text{O}_2 \),\(^10\) The treatment by \( \text{H}_2 \) reduction and subsequent \( \text{O}_2 \) oxidation is indispensable for activation of the \( \text{NiO} / \text{SrTiO}_3 \) photocatalyst. The \( \text{NiO} \) co-catalyst for \( \text{H}_2 \) evolution is particularly characteristic because it does not cause the back reaction between \( \text{H}_2 \) and \( \text{O}_2 \) being different from Pt. The excellent \( \text{NiO} \) co-catalyst has often been employed also for other photocatalysts for...
Akihiko KUDO  

water splitting. Besides the titanate photocatalysts, ZrO$_2$\(^{12}\) and NiO/\(Ti_2O_3\)\(^{13}\) have been reported to show high activities. These photocatalysts possess simple crystal structure without any characteristic secondary structure. In contrast to them, microporous crystals such as layered compounds have been applied to photocatalysts because they supply unique reaction sites.\(^{18}, 19\) K$_4$Nb$_6$O$_{17}$ with layered structure as seen in mica and K$_2$La$_2$Ti$_3$O$_{10}$ with layered perovskite structure show high activities.\(^{4}, 14, 15\) K$_4$NbO$_{17}$ possesses two kinds of interlayers in which ion-exchangeable potassium cations exist as shown in Fig. 3. H$_2$ evolution proceeds in one interlayer with a nickel co-catalyst while O$_2$ evolution does in another interlayer. It is the characteristic of the K$_4$Nb$_6$O$_{17}$ photocatalyst that H$_2$ evolution sites are separated from O$_2$ evolution sites by the photoactive niobate layers.

A$_2$Ti$_n$O$_{2n+1}$ (A=Na, K, and Cs),\(^{20, 21}\) CsTi$_2$NbO$_7$,\(^{22}\) KCa$_2$Nb$_5$O$_{15}$,\(^{23}\) KLa$_n$Nb$_3$O$_{10}$,\(^{24}\) and Na$_2$W$_4$O$_{13}$\(^{24}\) photocatalysts with layered structure are also active for H$_2$ or O$_2$ evolution from aqueous solutions in the presence of sacrificial reagents. These layered photocatalysts show luminescence and the excited energies are delocalized more or less.\(^{25, 26}\) Na$_2$Ti$_6$O$_{13}$\(^{16}\) and BaTi$_2$O$_5$\(^{17}\) with tunnel structure are also unique photocatalysts.

4. Tantalate photocatalysts for water splitting\(^{27)-35}\)

Although the development of photocatalysts has extensively been studied, the photocatalyst material is still limited. Many photocatalysts are titanates. So, it is important to develop new photocatalyst materials. New photocatalyst materials, except for titanates, have been surveyed by the author’s group with paying attention to structural regularity. K$_3$Ta$_2$Si$_3$O$_{13}$ with pillared structure was found to be active for water splitting without any co-catalyst.\(^{27}\) Moreover, the activity drastically increased with loading a small amount of a NiO co-catalyst. This result has lead us to investigate photocatalytic activities over other tantalates.\(^{28)-31}\) Alkali and alkaline earth tantalates showed photocatalytic activities for water splitting into H$_2$ and O$_2$ as shown in
Table 2. LiTaO₃ was the most active among the naked alkali tantalates. Among tantalates tested in the present study, NiO-loaded NaTaO₃ was most active. 29) The photocatalytic activity of NiO/NaTaO₃ increased with La-doping. 29) Water splitting into H₂ and O₂ proceeded with a quantum yield of about 50% as shown in Fig. 4. Highly crystalline particles of non-doped and La-doped NaTaO₃ were observed by scanning electron microscopy as shown in Fig. 5. The particle size of La-doped NaTaO₃ was 0.1-0.7 µm, while that of non-doped NaTaO₃ was 2-3 µm. Step structure was observed on the surface of La-doped NaTaO₃, whereas the surface of non-doped NaTaO₃ was flat. The decrease in the particle size and the creation of the step structure by the La-doping probably cause the high photocatalytic activities.

Sr₂Ta₅O₁₄ with layered perovskite structure also showed a high photocatalytic activity. 31) The photocatalytic activity of Sr₂Ta₅O₁₄ was higher than that of Sr₂Nb₂O₇ with the similar structure. Activation treatment was not necessary for NiO/Sr₂Ta₅O₁₄ while the pretreatment was indispensable for the NiO/Sr₂Nb₂O₇ photocatalyst. The difference in the photocatalytic properties between tantalates and niobates is mainly due to the conduction band levels (Ta 5d and Nb 4d) and distortion in connection between the MO₆ octahedra.

Zr, Ti, and Hf-doped KTaO₃, 33) RbNdTa₂O₇ with layered perovskite structure, 34) and K₂LnTa₅O₁₅ with tungsten bronze structure 35) are also new tantalate photocatalysts for water splitting.

5. BiVO₄ photocatalyst prepared by an aqueous process for O₂ evolution under visible light irradiation 36), 37) Some photocatalysts with wide band gaps have been reported to be highly active for splitting water into H₂ and O₂ in stoichiometric amounts under UV irradiation as mentioned above. The final goal of the present research field is the development of photocatalysts efficiently working under solar light irradiation for water splitting into H₂ and O₂. In the present stage, however, even in the presence of sacrificial reagents, the well-known photocatalysts which are active under visible light irradiation are only Pt/CdS for H₂ evolution and WO₃ for O₂ evolution. Therefore, the development of new visible-light-driven photocatalysts has strongly been urged.

The valence band of most oxide semiconductor photocatalysts consists of O 2p orbitals. 38) The valence band

Table 2. Water Splitting over Alkali and Alkaline Earth Tantalate Photocatalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Band gap / eV</th>
<th>NiO loaded / mass%</th>
<th>Activity / µmol/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiTaO₃</td>
<td>4.7</td>
<td>None</td>
<td>430</td>
</tr>
<tr>
<td>LiTaO₃</td>
<td>4.7</td>
<td>0.10</td>
<td>98</td>
</tr>
<tr>
<td>NaTaO₃</td>
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<td>160</td>
</tr>
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<td>0.05</td>
<td>2180</td>
</tr>
<tr>
<td>KTaO₃</td>
<td>3.6</td>
<td>None</td>
<td>29</td>
</tr>
<tr>
<td>KTaO₃</td>
<td>3.6</td>
<td>0.10</td>
<td>7.4</td>
</tr>
<tr>
<td>CaTa₂O₆</td>
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<td>None</td>
<td>21</td>
</tr>
<tr>
<td>CaTa₂O₆</td>
<td>4.0</td>
<td>0.10</td>
<td>72</td>
</tr>
<tr>
<td>SrTa₂O₆</td>
<td>4.4</td>
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<td>140</td>
</tr>
<tr>
<td>SrTa₂O₆</td>
<td>4.4</td>
<td>0.10</td>
<td>960</td>
</tr>
<tr>
<td>BaTa₂O₆</td>
<td>4.1</td>
<td>None</td>
<td>33</td>
</tr>
<tr>
<td>BaTa₂O₆</td>
<td>4.1</td>
<td>0.30</td>
<td>629</td>
</tr>
</tbody>
</table>

Alkali tantalates were prepared in the presence of excess amounts (5%) 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.
levels are about +3 V (vs. NHE) which is deep enough to oxidize H2O to O2. It causes oxide semiconductor photocatalysts to have wide band gaps. It is necessary to make a valence band consisting of an orbital other than O 2p to develop new visible-light-response photocatalyst materials. Here, Bi3+ with 6s2 configuration attracted our attention as a candidate which can form such a valence band.

BiVO4 with scheelite (monoclinic) structure, which was prepared by a conventional solid state reaction between NH4VO3 and Bi2O3 powder at 1170 K, was found to show a photocatalytic activity for O2 evolution from an aqueous silvery nitrate solution under visible light irradiation (λ>420 nm) via a scheme as shown in Fig. 1 (C). Therefore, the preparation method has been investigated to obtain highly active BiVO4 photocatalyst.

BiVO4 powders were synthesized by simply stirring vanadate powder such as K3V5O14 and Bi(NO3)3·5H2O powder as a dispersion in water at room temperature for 3 days. Highly crystalline BiVO4 powders with the scheelite (monoclinic) and zircon type (tetragonal) structure were selectively synthesized by changing the ratio of vanadium to bismuth in the starting materials as shown in Fig. 6. The single phases of the scheelite (monoclinic) and zircon type (tetragonal) structure were confirmed by X-ray diffraction. Diffuse reflectance spectra of BiVO4 are shown in Fig. 7. The zircon type BiVO4 with a 2.9 eV band gap mainly showed an ultraviolet absorption band while the scheelite BiVO4 with a 2.4 eV band gap had a characteristic visible light absorption band in addition to the UV band. The UV bands observed in the zircon type and scheelite BiVO4 were assigned to the band transition from O 2p to V 3d whereas the visible light absorption was due to the transition from

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**Fig. 5.** Scanning electron micrographs of non-doped and La-doped NaTaO3 powder.
(a) Non-doped, (b) La-doped.

**Fig. 6.** Scanning electron micrographs of BiVO4 prepared by an aqueous process at room temperature.
(a) Scheelite structure (monoclinic), (b) Zircon type structure (tetragonal).

**Fig. 7.** Diffuse reflectance spectra of BiVO4 prepared by an aqueous process at room temperature.
(a) Scheelite structure (monoclinic), (b) Zircon type structure (tetragonal).
the valence band formed by a hybrid orbital of Bi 6s and O 2p to the conduction band consisting of V 3d. The scheelite BiVO₄ showed a high photocatalytic activity for O₂ evolution from an aqueous silver nitrate solution under visible light irradiation. The photocatalytic activity of BiVO₄ was much higher than that of the commercial WO₃ with a 2.8 eV band gap which is a well-known photocatalyst for O₂ evolution reaction under visible light irradiation as shown in Fig. 8. The maximum quantum yield at 450 nm was 9% for the scheelite BiVO₄.

The photocatalytic activity of the scheelite BiVO₄ prepared by the aqueous process was much higher than that of the scheelite BiVO₄ prepared by a conventional solid state reaction even in the same crystal structure. The difference in the photocatalytic activity between BiVO₄ obtained by the different methods is due to the crystallinity and defects. It is noteworthy that obtaining the highly crystalline powder without significant formation of defects and the decrease in the surface area by the aqueous process at room temperature led to the development of a highly active photocatalyst working under visible light irradiation. It means that the aqueous process is especially advantageous for the preparation of materials in which defects are easily formed by volatilization at high temperatures.

6. Modified ZnS photocatalyst for H₂ evolution under visible light irradiation

Zinc sulfide is one of well-known photocatalysts. It is highly active for hydrogen evolution in the presence of sacrificial reagents even without co-catalysts such as platinum. It means that the conduction band level is high enough to reduce H₂O to H₂, and moreover, the surface possesses a catalytic ability for H₂ formation. However, it responds to only UV light because the band gap is 3.7 eV. It will be interesting if a new valence band can be formed to decrease the band gap with keeping the high ability for H₂ evolution. Hence, the possibility of development of zinc sulfide-based photocatalysts for H₂ evolution from aqueous solutions under visible light irradiation was explored.

Cu²⁺ and Np⁺-doped zinc sulfide photocatalysts were prepared by co-precipitation method. The Zn₀.₉₉₉Nι₀.₀₀₁S photocatalyst was heat-treated under N₂ flow at 770 K. Figure 9 shows H₂ evolution from aqueous potassium sulfite and sodium sulfide solutions on Zn₀.₉₅₇Cu₀.₀₄₃S and Zn₀.₉₉₉Nι₀.₀₀₁S photocatalysts under visible light irradiation via a scheme as shown in Fig. 1 (b). The quantum yields at 420 nm were 7.5 and 1.3%, respectively. It is noteworthy that these photocatalysts showed such a high activity without co-catalysts such as platinum. It means that the photocatalyst possesses good catalytic sites and sufficiently high conduction band levels for H₂O reduction to form H₂ as well as a non-doped zinc sulfide photocatalyst.

Figure 10 shows diffuse reflectance spectra of Zn₀.₉₅₇Cu₀.₀₄₃S, Zn₀.₉₉₉Nι₀.₀₀₁S, and non-doped ZnS. The energy gaps of Zn₀.₉₅₇Cu₀.₀₄₃S and Zn₀.₉₉₉Nι₀.₀₀₁S were estimated to be 2.5 and 2.3 eV, respectively, from the onsets. The color of these compounds was pale yellow. The absorption spectra of Zn₀.₉₅₇Cu₀.₀₄₃S and Zn₀.₉₉₉Nι₀.₀₀₁S consist of two bands: one is a visible light absorption band and the another is a UV absorption band. The UV band originates that of ZnS. The visible light absorption bands are due to the transition from doped Cu²⁺ and Np⁺ to the conduction band of zinc sulfide.

7. Photocatalyst materials consisting of d¹⁰ ions

Photocatalysts for water splitting consist of s-block ions and Ti⁴⁺, Zn²⁺, Nb⁵⁺, and Ta⁵⁺ with d⁰ configuration as shown in the Chapters 3 and 4. In the Chapter 5, it was indicated that a p-block cation of Bi³⁺ plays an important role for the formation of band structure. Therefore, photocatalytic activities of materials consisting of p-block ions with d¹⁰

Fig. 10. Diffuse reflectance spectra of Zn₀.₉₅₇Cu₀.₀₄₃S, Zn₀.₉₉₉Nι₀.₀₀₁S, and ZnS.

(a) Zn₀.₉₅₇Cu₀.₀₄₃S, (b) Zn₀.₉₉₉Nι₀.₀₀₁S, (c) ZnS.
and/or \( s^2 \) configuration were investigated as shown in Table 3.

An activated NiO/ZnNb\(_2\)O\(_6\) catalyst produced \( \text{H}_2 \) and \( \text{O}_2 \) from pure water.\(^{42} \) Niobate photocatalysts which are active for water splitting were only \( \text{K}_4\text{Nb}_6\text{O}_{17} \)\(^{14} \), \( \text{Sr}_2\text{Nb}_2\text{O}_7 \)\(^{3} \), \( \text{ZnNb}_2\text{O}_6 \) with layered structure. \( \text{ZnNb}_2\text{O}_6 \) is a new type of photocatalyst materials from the view point of the component because it consists of \( d^{10} \) and \( d^0 \) metal ions.

Solid solutions of \( \beta\)-Ga\(_2\)O\(_3\) and In\(_2\)O\(_3\) consisting of \( d^{10} \) cations showed photocatalytic activities for \( \text{H}_2 \) or \( \text{O}_2 \) evolution from aqueous solutions in the presence of sacrificial reagents.\(^{43} \) In this photocatalyst system, the band gap and luminescent energy decreased as a ratio of indium increased. Homologous \( \text{In}_2\text{O}_3(\text{ZnO})_n \) compounds showed photocatalytic activities under visible light irradiation.\(^{44} \) \( \text{Bi}_2\text{WO}_6 \), \( \text{Bi}_2\text{WO}_6 \), and \( \text{Bi}_2\text{TiNb}_3\text{O}_9 \) consisting of layered structure with perovskite slabs interleaved with \( \text{Bi}_2\text{O}_2 \) layers showed photocatalytic activities for \( \text{H}_2 \) or \( \text{O}_2 \) evolution from aqueous solutions.\(^{45} \) \( \text{Bi}_2\text{WO}_6 \) with the Aurivillius structure and a 2.8 eV band gap was active for an \( \text{O}_2 \) evolution reaction under visible light irradiation.

8. Conclusion

\( \text{NiO/NaTaO}_3\): La was found to be a highly active photocatalyst for water splitting, very tough reaction under UV light irradiation. This result has proven that highly efficient water splitting is actually possible using a photocatalyst system. Moreover, although a sacrificial reagent is needed, \( \text{BiVO}_4 \) was found to be active for \( \text{O}_2 \) evolution under visible light irradiation. The photocatalytic activity of \( \text{BiVO}_4 \) was improved by the development of a new synthesis method in aqueous media. In the \( \text{BiVO}_4 \) photocatalyst, Bi 6s orbitals seem to play an important role for controlling the valence band. \( \text{Zn}_{0.097}\text{Cu}_{0.903}\text{S} \) and \( \text{Zn}_{0.999}\text{Ni}_{0.001}\text{S} \) of new visible-light-response photocatalysts for \( \text{H}_2 \) evolution were also developed. The development of the zinc sulfide-based photocatalysts is expected to give some information on making UV-response photocatalysts respond to visible light. The results introduced in the present review are expected to throw a light on the further development of photocatalyst materials for artificial photosynthesis and solar light energy conversion in the 21st century.

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References

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