

2-1-1. Water Splitting

Overview

Since the discovery of the Honda-Fujishima effect in the late 1960s, research on water splitting using photocatalysts and semiconductor photoelectrodes has been conducted worldwide. Recently, attention has focused on the development of photocatalysts capable of water splitting using visible light. Various kinds of visible-light-responsive water-splitting photocatalysts have been developed. For an overview up to the 1990s, refer “2-1-1. Water splitting” in the Photochemistry Div Report described in Japanese. URL: <https://division.csj.jp/div-report/02/0220101.pdf>

Current Status and Frontiers

Water splitting using a powdered photocatalyst is characterized by its simple system, low cost, and relatively easy large-area deployment. The photocatalyst system is divided into single-particle photocatalysts and Z-scheme photocatalysts, as shown in Fig. 1. Here, water splitting refers to the reaction that splits water into hydrogen and oxygen in a 2:1 ratio using light energy. This is distinct from hydrogen production using an electron donor (sacrificial reagent) (see “2-1-2. Photohydrogen Production”). Furthermore, active research is being conducted on the generation of H_2O_2 instead of O_2 as a water oxidation product.

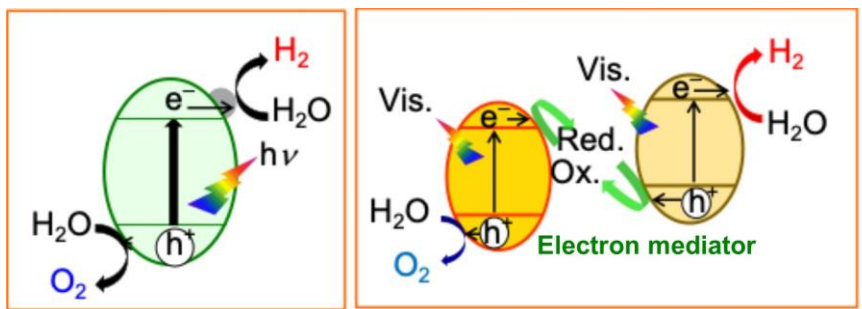


Figure 1. Single particulate photocatalyst and Z-scheme photocatalyst.

1. Single-particle photocatalysts

Numerous single-particle photocatalysts active in water splitting under UV light have been reported. However, visible-light-responsive photocatalysts are extremely limited. Although a UV-sensitive photocatalyst, Domen *et al.* demonstrated water splitting using sunlight at 100 m^2 using a Rh-CrOx/SrTiO₃:Al powder photocatalyst. This demonstrates world-class performance for a powder photocatalyst. As a visible-light responsive metal oxide photocatalyst, SrTiO₃ co-doped with Ir, Rh, Ru, or Cr and Sb

exhibits high activity for water splitting when used with a Rh-CrO_x cocatalyst. Among these, SrTiO₃:Ir responds to visible light up to 600 nm. On the other hand, oxynitrides and oxysulfides whose N2p and S3p orbitals form valence bands often absorb visible light compared to metal oxides. For example, GaN-ZnO, LaMg_{1/3}Ta_{2/3}O₂N, Ta₃N₅, SrTaO₂N, Y₂Ti₂O₅S₂ loaded with appropriate cocatalysts are active in visible-light water splitting. Some of these photocatalysts respond to visible light up to around 600 nm.

2. Z-scheme photocatalyst

Z-scheme photocatalysts can be constructed with materials that are active in either hydrogen or oxygen production using a sacrificial reagent. SrTiO₃:Rh of a H₂-evolving photocatalyst and BiVO₄ of an O₂-evolving photocatalyst have excellent properties and are widely used. In addition, metal oxides such as SrTiO₃:Cr, BaTa₂O₆:Ir, La, metal sulfides such as (CuGa)_{0.5}ZnS₂, Cu₃VS₄, and metal oxysulfides and selenides such as Sm₂Ti₂S₂O₅, Ga-La₅Ti₂CuS₅O₇, (ZnSe)_{0.5}(CuGa_{2.5}Se_{4.25})_{0.5} are known as H₂-evolving photocatalysts. Metal oxides such as WO₃, SrTiO₃:Ru, TiO₂:Rh, Sb, oxynitrides such as Ta₃N₅, TaON, GaN:ZnO, and oxyhalides such as Bi₄NbO₈Cl are also often used as O₂-evolving photocatalysts. By combining these photocatalysts with appropriate electron mediators such as Fe^{3+/2+}, Co^{3+/2+} complexes, reduced graphene oxide, polyoxometalate ions, the conductive polymer PEDOT, and gold, many types of Z-scheme photocatalysts active in visible light water splitting have been constructed.

References

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2. J. Xiao, T. Hisatomi, K. Domen, *Acc. Chem. Res.*, **56**, 878–888 (2023).
3. H. Nishiyama, K. Domen, et al., *Nature*, **598**, 304–307 (2021).
4. A. Kudo, et al., *Faraday Discuss.*, **215**, 313–328 (2019).
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Future Perspectives and Directions

As the first step toward practical application in society, it is essential to develop powdered photocatalyst materials with a solar-to-hydrogen energy conversion efficiency (STH) of over 5%. To achieve this, it is essential to improve efficiencies of existing photocatalysts and develop new photocatalysts.

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