2-1-2. Photochemical Hydrogen Production

Overview

Green hydrogen production by water splitting has been discussed in "2-1-1. Water Splitting". Here, we describe visible-light-responsive H_2-evolving photocatalysts that are active in the presence of an electron donor (sacrificial reagent) but not in water splitting. In recent years, a lot of metal oxide, metal oxynitride, and chalcogenide visible-light-responsive photocatalysts with high quantum yields have been developed. The development of these photocatalysts is important from the perspective of their potential use as Z-scheme H_2-evolving photocatalysts and photocathodes, as shown in Fig. 1.

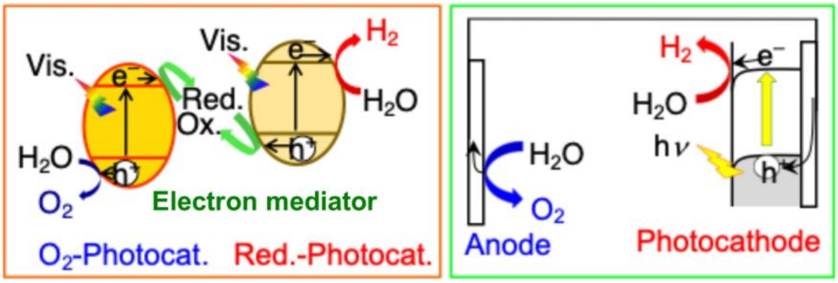

Figure 1. Application of H_2-evolving photocatalyst to Z-scheme photocatalyst and photocathode.

Current Status and Frontiers

CdS and CdS-ZnS have long been widely studied as visible-light-responsive photocatalysts that produce hydrogen in the presence of a sacrificial reagent. However, these metal sulfides have n-type properties and cannot be used as photocathodes, which require p-type properties, as shown in Fig. 1. Cu_2O and NiO are known as p-type semiconducting metal oxides, but photocorrosion due to light exposure in aqueous solution, particularly Cu_2O, poses a significant challenge. In addition to this, in recent years, a wide variety of photocatalysts have been developed through various band engineering techniques.

While $SrTiO_3$ is n-type, doping it with Rh not only makes it visible light responsive, but also photoelectrochemically p-type. This $SrTiO_3$:Rh exhibits high activity for H_2 generation when irradiated with visible light in the presence of a sacrificial material, and can be used in Z-scheme visible light-responsive hydrogen generation photocatalysts and hydrogen generation photocathodes as shown in Fig. 1.

Among metal sulfides, $ZnIn_2S_4$, ZnS:M (M = Cu, Ni, Pb), $(ZnS)_{0.9}$-$(CuCl)_{0.1}$, $CuGaS_2$,

$AgGaS_2$, Cu_2ZnGeS_4, Ag_2ZnGeS_4, Ag_2ZnSnS_4, $CuGaGeS_4$, $CuGa_5S_8$, Cu_3VS_4, Cu_3NbS_4, Cu_4TiS_4 have been found to be visible-light-responsive H_2-evolving photocatalysts. In addition, solid solutions of these metals, such as $CuInS_2$-$AgInS_2$-ZnS, $CuGaS_2$-ZnS, $CuGaS_2$-$AgInS_2$, also exhibit activity. Solid solution photocatalysts have the advantage that the conduction band and valence band levels, and therefore the band gap, can be freely tuned by changing the solid solution ratio. This band engineering has also led to the synthesis of colloids with tunable emission colors. Metal sulfides containing Cu as a constituent element often exhibit p-type characteristics, and Cu_2ZnGeS_4, Cu_2ZnSnS_4, Cu_3VS_4, $(CuGa)_{1-x}Zn_{2x}S_2$, $(CuGa)_xZn_{1-2x}In_2S_4$ have been reported to function as Z-scheme H_2-evolving photocatalysts and photocathodes for hydrogen production and carbon dioxide reduction. Oxynitride photocatalysts such as GaN:ZnO, $LaTiO_2N$, TaON, $BaTaO_2N$, and oxysulfide photocatalysts such as $Sm_2Ti_2O_5S_2$, $Y_2Ti_2O_5S_2$ have been reported.

References

1. A. Kudo, Y. Miseki, *Chem. Soc. Rev.*, **38**, 253–278 (2009).
2. A. Kudo, *Electrochemistry*, **93**, 101001 (2025).
3. K. Iwashina, A. Kudo, *J. Am. Chem. Soc.*, **133**, 13272–13275 (2011).
4. T. Torimoto, T. Adachi, K. Okazaki, M. Sakuraoka, T. Shibayama, B. Ohtani, A. Kudo, S. Kuwabata, *J. Am. Chem. Soc.*, **129**, 12388–12389 (2007).
5. K. Maeda, H. Kageyama, et al., *Bull. Chem. Soc. Jpn.*, **95**, 26–37 (2022).

Future Perspectives and Directions

The hydrogen production reaction from an aqueous solution containing a sacrificial reagent can be considered a half-reaction of water splitting. Therefore, these photocatalysts should be further developed for artificial photosynthetic uphill reactions using Z-scheme systems or photocathode systems. Although photocatalysts exhibiting high quantum yields in the presence of sacrificial reagents have been developed, their high performance has not yet been fully realized when used in Z-scheme systems. This is thought to be due to the significant inhibiting effects of back electron transfer and reverse reactions. It is necessary to find a solution to this problem. If this can be achieved, it is expected to make a significant contribution to green hydrogen production.

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