Water Splitting for H_2 Production using Visible-light-responsive Photocatalysts

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Abstract

Photocatalytic water splitting using semiconductor materials has attracted considerable interest due to its potential for clean production of H_2 from water through the conversion of abundant solar energy into chemical energy. This article briefly analyzed the trend and progress in the research and development of visible-light-responsive photocatalysts for water splitting in the past few years. Particularly, metal sulfides and composite photocatalysts were discussed. This brief review article aims at facilitating a search of stable and efficient photocatalysts for water splitting, and revealing fundamental insight into the development of novel visible light-adsorbing photocatalysts.

Keyword: water splitting, visible light, hydrogen production, metal sulfide

Hydrogen (H_2) production using visible-light photocatalyst for water splitting has attracted considerable attention due to the growing demand for environmentally friendly and sustainable energy sources. The number of journal articles on water splitting for H_2 production dramatically increased over the past few years (Fig.1), highlighting the tremendous interests in photocatalytic water splitting as a means of producing renewable clean energy production with minimum carbon footprint. Since the early 1970s, intensive efforts have been directed toward research and development of various photocatalytic materials for water splitting for H_2 production. Most traditional photocatalysts, such as TiO_2 and $ZnGa_2O_4$, have relatively large band gaps and thus can capture only ultraviolet (UV) irradiation, which accounts for a small fraction of solar irradiation. To overcome this limitation, many types of visible-light-absorbing materials with narrower band gaps, such as mixed oxides, oxynitride, and metal sulfides[1-3], are developed as shown in Fig. 2. Until today, developing visible light photocatalysts remains the focus in this field. As shown in Fig. 1, the number of journal articles on visible light-driven photocatalyst between 2006 and 2010 is almost 5 times the number of journal articles published between 1981 and 1985. It is also worth noting that before 2000, the publications on water splitting under UV irradiation outnumbered those under visible light. By contrast, after 2000, much more attention is being directed toward water splitting under visible light, especially in the past five years. Moreover, the number of journal articles on UV driven water splitting has declined over that past 5 years.

This article compared the quantum yield (QY) and H_2 productivity in different novel visible-light–adsorbing photocatalytic systems that were developed in the past few years. This article also examined the colloidal stability or durability, quantum efficiency, and potential environmental impacts between different studies, which laid groundwork toward developing and designing new rationale

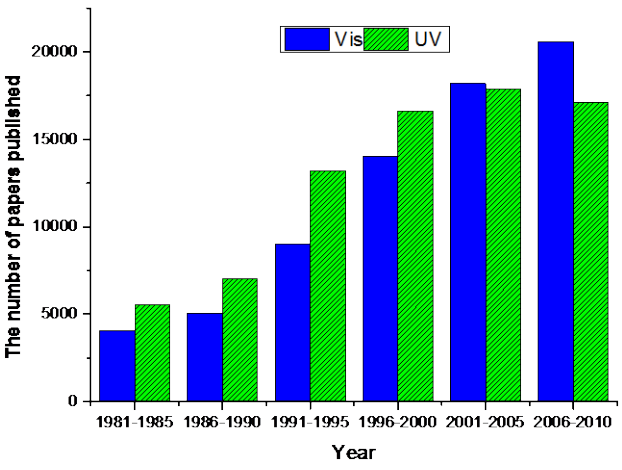

Fig. 1. The number of journal articles on water splitting published with years. VIS: visible light. UV: ultraviolet.

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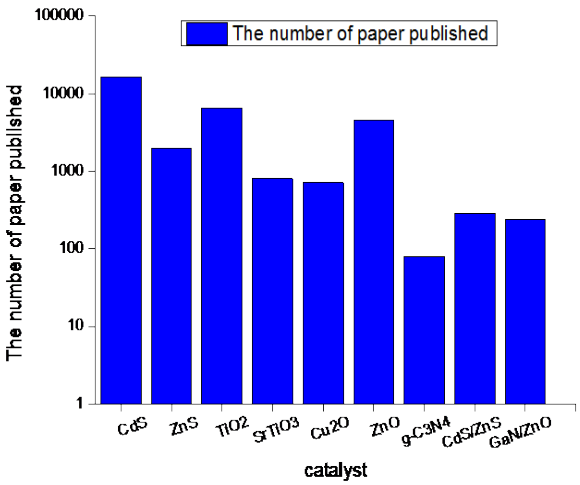

Fig. 2. The number of journal articles on different popular visible-light-responsive photocatalysts published from 2007 to 2012.

visible-light-responsive photocatalysts.

1. Visible light-driven metal sulfide photocatalyst for water splitting

Metal sulfides are attractive materials as candidates of visible light-driven photocatalysts due to the narrow band gaps and negative valence band potentials. Despite the excellent visible-light photocatalytic activity, they often exhibit poor photostability and undergo photocorrosion with prolonged light illumination. Yet the photocorrosion can be suppressed in the presence of sacrificial reagents. Many metal sulfide photocatalysts have been successful for H_2 evolution in the presence of sacrificial reagents as demonstrated in Table 1. For instance, CdS is one of the most popular photocatalysts,[2, 4] because of its appropriate band gap (2.4eV) and electronic structures (e.g., the conduction band is -0.9 eV in reference to NHE at PH=7, the valence band is +1.5 eV in reference to NHE at PH=7). Different photocatalysts led to dramatically different QYs for different systems (Table 1). In addition, it is actually challenging to quantitatively compare the H_2 production efficiency and productivity due to the lack of a common measure or indicator. So, H_2 productivity expressed with different units (i.e., μmol/h, μmol/mg/h, and μmol/m^2/h) were proposed and calculated in Table 1. Due to the availability of data or experimental details in the reference articles, we were able to obtain some of the H_2 productivity quantities, which appeared to vary significantly with photocatalytic systems. Yan et al. reported that a quantum yield of 93% at 420 nm using the Pt-PdS/CdS photocatalyst in the presence of the sacrificial reagent of Na_2S and Na_2SO_3 , which is the highest photocatalytic activity so far.[2] Accordingly, its H_2 productivity seems to be the highest. However, Graphene-CdS and CdSeZnS/Zr/Ti/phosphate, if evaluated by the H_2 production rate per unit photocatalyst mass, would apparently yield much greater H_2 than Pt-PdS/CdS. Thus, it is important develop holistic evaluation methods to access the H_2 productivity for different photocatalytic systems.

2. Water splitting for H_2 production using composite photocatalysts

Clearly, efficient photocatalytic water-splitting systems require stable photocatalysts that have photocatalytic activity with repeated consecutive use. Most recently, many efforts have focused on the design of novel semiconductor materials and the optimization of chemical composition and microstructures to increase the photostability and quantum yield. For example, multicomponent sulfides, such as $ZnIn_2S_4$,[5, 6] and $(CuAg)_xIn_{2x}Zn_{2(1-2x)}S_2$ [7, 8] have been studied as a new class of visible-light-driven photocatalysts for water splitting and H_2 production.[9] Zhang *et al*., recently developed a visible light-responsive photocatalyst ($Ru/(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$) and successfully achieved H_2 evolution in the presence of KI as the sacrificial reagent.[10]. The study also examined the kinetics of photocatalytic generation of H_2, stability and reusability of the catalyst over multiple cycles of H_2 production and catalyst regeneration, which is not commonly reported elsewhere. The examination of stability and longevity of photocatalytic H_2 production is important and necessary to quantitatively compare the actual H_2 productivity from different photocatalytic systems.

The photocatalyst reported by Zhang et al was well-crystallized particles (30–50 nm in diameter) with high photocatalytic activity and broad visible light absorbance (from 400 nm up to 650 nm). The highest H_2 production rate was approximately 190 ± 6.5 μmol·h^{-1} at the initial pH of 4

and 0.2 M KI as electron donor. The highest $QY^{415–425}$ (QY under the wavelength of 420±5 nm) was 4.6 ± 0.3%. Although this QY does not seem to be stunning and even lower than those of some similar catalysts, such as Pt/CdS ($QY^{415–425} \approx 24\%$),[11] and $(CuAg)_{0.15}In_{0.3}Zn_{1.4}S_2$ ($QY^{415–425} \approx 7\%$),[8] the catalyst exhibited relatively good colloidal stability and was able to capture a wide spectrum of the solar irradiation (400–650 nm). Most importantly, this article provided systematic investigations on the longevity of the photocatalyst with consecutive reaction cycles. The study monitored the particle size distribution and metal ion release during the photocatalytic H_2 production, which help understand why the H_2 production rate decreased from 190 to 120 $\mu mol \cdot h^{-1}$ with over different reaction cycles. It was experimentally observed that the photocatalyst particles underwent pronounced aggregation, which led to the increase in particle size; and a significant release of metal ions was observed during H_2 production, which led to a loss of the catalyst mass and potential changes in the photocatalytic activity. Consequently, these processes may result in the decrease of photocatalytic activity and stability.

3. Conclusion

Solar water splitting for H_2 production is important to obtain clean energy in the future. Nowadays, there are many photocatalysts have been developed, and the focus is largely on the novel material synthesis and improvement of photocatalytic activity. In the future, it is necessary to take the stability and reusability of photocatalysts into consideration. In addition, applications of photocatalyst materials made of earth abundant elements would be more attractive and critical for energy sustainability.

Table 1. Comparison of hydrogen evolution with different visible light-responsive photocatalysts

Catalyst	Light source	QY	H_2 Productivity			Ref.
		%	μmol/h	μmol/mg/h	$\mu mol/m^2/h$	
$Pt/CdS/TiO_2$	N.A.	20	54	0.68	N.A.	[1]
Pt-PdS/CdS	≥420 nm	93	8770	29.23	N.A.	[2]
$Pt/[In(OH)_yS_z]$:Zn	≥420 nm	0.59	67	0.22	N.A.	[12]
PPy/CdS	≥430 nm	N.A.	110	0.73	N.A.	[13]
Graphene-CdS	420 nm	22.5	1120	556	N.A.	[14]
CdSeZnS/Zr/Ti/phosphate	420 nm	9.6	714	35.71	N.A.	[15]
CdS/TiO_2	420 nm	43.4	402	N.A.	N.A.	[16]
$(Cd_{0.8}Zn_{0.2})S$	≥420 nm	N.A.	302	3.02	N.A.	[17]

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