ENABLING ZNIN2S4 PHOTOCATALYSTS TO ACHIEVING REDOX-DRIVEN OVERALL WATER SPLITTING UNDER VISIBLE LIGHT

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ABSTRACT

While metal sulfides are good candidates as visible light responsive photocatalysts for solar-driven hydrogen evolution, it is still challenging to implement in overall water splitting due to severe self-photooxidation. Construction of a Z-scheme system is a useful strategy to split water into H_2 and O_2 using such photocorrosive metal sulfides because the photogenerated holes in metal sulfides are efficiently transported away. Here, we show that modification of $ZnIn_2S_4$ with designed cocatalysts and oxide coatings enable stable overall water splitting, when the sulfides are used in combination with a $BiVO_4$-based O_2 evolution photocatalyst and $[Fe[CN]_6]^{3-}/[Fe[CN]_6]^{4-}$ redox mediator, relative to an analogous system that used unmodified $ZnIn_2S_4$. By using the optimized photocatalyst, this system can achieve high hydrogen production activity under visible light and shows almost no decay in a 12-hour cyclic test.

KEY WORDS

Photocatalyst; Sulfide; Water splitting; Redox mediator; Hydrogen evolution

INTRODUCTION

Photocatalytic overall water splitting is a promising method for directly converting solar energy into hydrogen energy with no reliance on fossil fuels and no carbon dioxide emission, which is beneficial for address the increasing demand for energy and associated environmental concerns.[1,2] In contrast to sacrificial hydrogen production, overall water splitting offers economic benefits due to the elimination of the need for supplementary sacrificial agents. Currently, the main approaches to photocatalytic overall water splitting are the one-step photoexcitation system and the two-step photoexcitation system, the latter often referred to as the Z-scheme system. The former method, which utilizes a single catalyst, faces more stringent thermodynamic and kinetic demands. Consequently, high efficiency has only been achieved in the ultraviolet range to date.[3] In the visible light range, there are very few photocatalysts capable of splitting water stoichiometrically via one-step photoexcitation, with efficiency being an even greater challenge. Given that nearly half of the solar energy that reaches the Earth falls within the visible light spectrum of 400-700 nm, achieving overall water splitting under visible light is crucial for improving the efficiency of converting solar energy into hydrogen energy.[4] The Z-scheme system employs a pair of photocatalysts, with one designated for hydrogen evolution and the other for oxygen evolution. They are linked through an electron mediator, enabling the directed transfer of electrons, in a manner that emulates the photosynthetic process of green plants. In contrast to the one-step photoexcitation system, the Z-scheme system imposes less thermodynamic restriction on materials and encompasses a wider spectrum of visible light absorption.[5] Therefore, it can be regarded as one of the optimal pathways for accomplishing overall water splitting utilizing visible light.

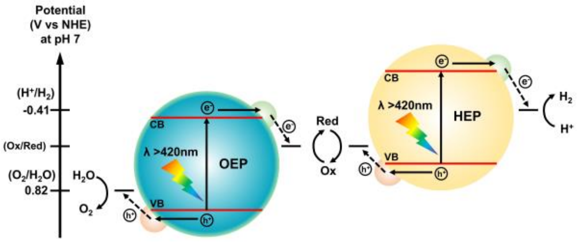

Fig.l: Schematic energy diagram of photocatalytic water splitting for the Z-scheme system under visible light.

Several high-performance visible-light Z-scheme systems have been reported to date, but the photocatalysts used for the hydrogen evolution are concentrated on doped oxides, (oxy)nitrides and oxysulfide.[6-8] However, metal sulfides are seldom utilized in Z-scheme overall water splitting systems, despite possessing a broad visible light absorption capability and excellent hydrogen production activity in the presence of sacrificial agents. Although solid-state Z-scheme systems using solid conductive media like graphene hold the potential to achieve efficient overall water splitting, it demands high standards for equipment and manufacturing processes to ensure efficient charge transfer between hydrogen evolution photocatalysts (HEPs) and oxygen evolution photocatalyst (OEPs).[9] Another approach to constructing a Z-scheme system is to use reversible ion pairs as an electron mediator to achieve directed electron flow from the OEP to the HEP, i.e., liquid-phase Z-scheme system. However, sulfides exhibit very low hydrogen evolution activity in the solutions containing redox couples. Despite the numerous reports on the hydrogen evolution half-reaction of sulfides currently available, most tests are conducted in the presence of strong electron donors such as lactic acid, Na_2S, and Na_2SO_3. There is limited research on the activity of sulfides in the solutions containing redox couples. Although it is challenging for a single sulfide to achieve overall water splitting, the aforementioned liquid-phase Z-scheme system may offer the potential to extend the research on sulfides, which has been primarily focused on the hydrogen evolution half-reaction for decades, into the field of overall water splitting.

In addition to performance, stability is also a key concern for the Z-scheme system, particularly for those based on sulfides. There are primarily two factors that affect stability. The first factor is the inherent susceptibility of sulfides to photocorrosion.[10] In the absence of sacrificial agents, photogenerated holes will oxidize the sulfide itself rather than water, causing structural damage to the material. The other factor is the oxygen generated during the reaction, which also has sufficient oxidizing power to cause the oxidation of the sulfide. Both of these factors can lead to the deactivation of the sulfide to varying degrees, thereby affecting the overall stability of the Z-scheme system. Hence, it is of significant importance to simultaneously mitigate the impact of these two factors on stability without compromising performance.

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