

# Construction of novel Z-scheme cobalt tetraphenylporphyrin/ZnIn<sub>2</sub>S<sub>4</sub> heterojunction for enhanced photocatalytic hydrogen evolution

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## ABSTRACT

Photocatalyst for water splitting is a promising method for producing clean hydrogen energy. The Z-scheme heterostructure photocatalysts have attracted considerable attention in recent years owing to the unique energy band structures and interfacial interactions. This work rationally constructed the cobalt tetraphenylporphyrin/ZnIn<sub>2</sub>S<sub>4</sub> heterostructure. The hydrogen evolution reaction (HER) activity of the 25% cobalt tetraphenylporphyrin/ZnIn<sub>2</sub>S<sub>4</sub> heterojunction was boosted considerably, reaching a maximum of 6.9 mmol h<sup>-1</sup> g<sup>-1</sup>, which is 1.8 times of the single ZnIn<sub>2</sub>S<sub>4</sub>. The increased separation efficiency of photogenerated carriers and visible light absorption are responsible for the high HER activity of the cobalt tetraphenylporphyrin/ZnIn<sub>2</sub>S<sub>4</sub> heterostructure. With the half-reactions using hole-sacrificing agents, this study constructed a reasonable Z-scheme heterostructure for efficient hydrogen evolution.

**Keywords:** Cobalt tetraphenylporphyrin, ZnIn<sub>2</sub>S<sub>4</sub>, hydrogen generation, photocatalyst

## 1. INTRODUCTION

Photocatalytic water splitting using solar energy is considered as one of the most promising ways for producing hydrogen in recent years [1, 2]. Photocatalytic hydrogen evolution technique has significant benefits in water resource pollution, environmental protection, and human health[3]. Nevertheless, there are still obstacles to efficient and steady hydrogen generation photocatalytic activity, and the main problems are the lack of absorption in the visible light spectrum from sunlight and the high frequency of photogenerated pairs.

ZnIn<sub>2</sub>S<sub>4</sub> is a promising semiconductor photocatalyst that benefits from being non-toxic, stable, inexpensive, and having a low band gap (2.2 eV) [4-7]. The shortage of this material is its low absorption capability on the visible light. Photosensitizers could help with this problem and porphyrins are essential ones existing in green plants photosynthesis [8], because they have high visible light absorption owing to their distinctive macrocyclic structure[9, 10]. It has been reported that cobalt porphyrin is photoactive photosensitizers and capable of delivering electrons between photocatalysts enabling redox reactions in different centers, making it a promising option for H<sub>2</sub> production [11, 12].

Therefore, in this study, a composite photocatalyst was prepared by modifying cobalt tetraphenylporphyrin on the surface of indium zinc sulfide. By modifying the cobalt tetraphenylporphyrin, the composite is able to absorb more photons when exposed to visible light, hence enhancing its photocatalytic hydrogen evolution ability. Moreover, the Z-scheme heterojunction structure helps enhance the separation of photogenerated carriers in semiconductor photocatalysts, leading to a more efficient evolution of hydrogen by photogenerated carriers' redox reaction[13]. The hydrogen generation activity was optimized by experimenting with various combinations of ZnIn<sub>2</sub>S<sub>4</sub> and cobalt tetraphenylporphyrin, and the underlying mechanism was explored.

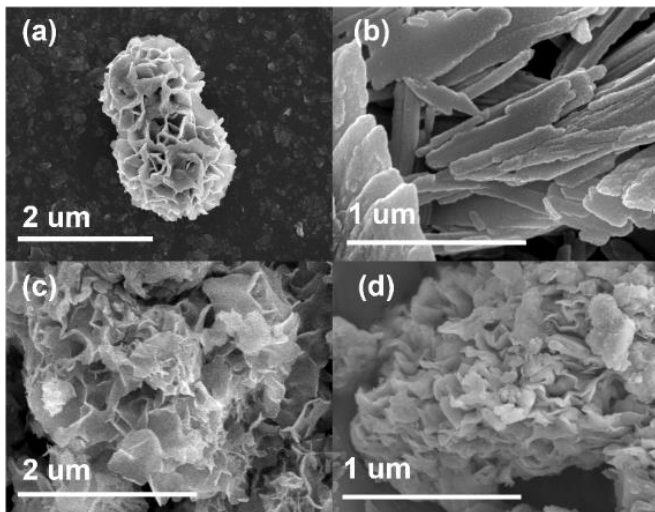
## 2. EXPERIMENT

### 2.1 Material and methods

ZnIn<sub>2</sub>S<sub>4</sub> and cobalt tetraphenylporphyrin was synthesized by a modified hydrothermal method respectively[14, 15]. The Cobalt tetraphenyl porphyrin/ZnIn<sub>2</sub>S<sub>4</sub> (porphyrin/ZnIn<sub>2</sub>S<sub>4</sub>) was fabricated by *in-situ* Friedel-Crafts alkylation hyper-crosslinking growth of cobalt tetraphenylporphyrin polymers on ZnIn<sub>2</sub>S<sub>4</sub> with different mass ratio.

## 2.2 Results and Discussion

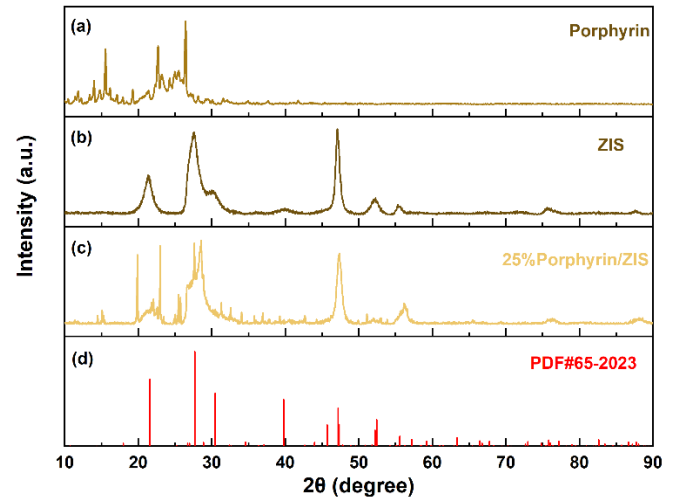
As shown in Fig. 2(a), the hydrothermally synthesized ZnIn<sub>2</sub>S<sub>4</sub> has a petal-like spherical shape with a diameter of approximately 1.5 μm. The sheet-like structure of cobalt tetraphenylporphyrin is depicted in Fig. 2(b). Fig. 2(c-d) show the morphology of the composite heterojunction ZnIn<sub>2</sub>S<sub>4</sub>/cobalt porphyrin, which is a multilayer structure resembling flower petal. The figures demonstrates that the two components are strongly coupled and have a high combined area, resulting in a stable composite structure that facilitates the migration of photoelectrons across the structures. In this heterojunction, the *in-situ* grown ZnIn<sub>2</sub>S<sub>4</sub> transitions from a spherical shape to a petal sheet shape, which is likewise favorable to photoelectron migration.



**Fig. 2.** SEM images of (a) ZnIn<sub>2</sub>S<sub>4</sub>, (b) Porphyrin, (c-d) 25% porphyrin/ZnIn<sub>2</sub>S<sub>4</sub> at different magnifications.

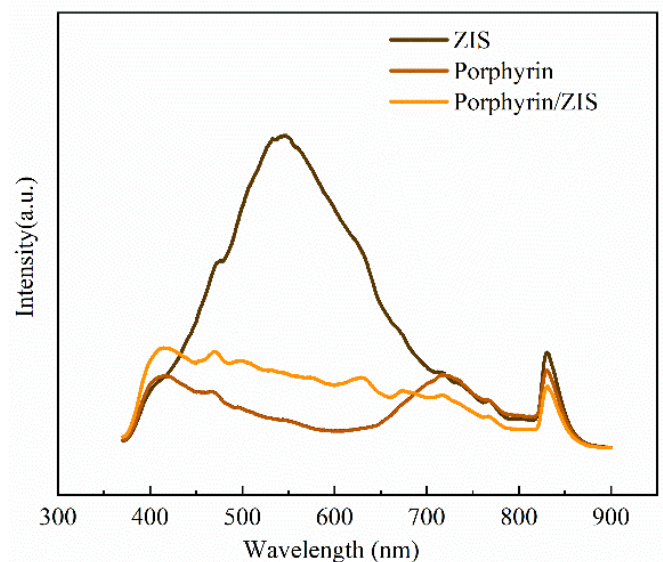
The high and narrow peaks in the XRD patterns seen in Fig. 2 indicate high crystallinity and purity of the produced materials. ZnIn<sub>2</sub>S<sub>4</sub> can be indexed as JCPDS PDF#65-2023, as ZnIn<sub>2</sub>S<sub>4</sub> in a spherical shape with a surface resembling petal, which is compatible with the SEM results of the synthesized samples. In comparison to the standard index, three major peaks of pure ZnIn<sub>2</sub>S<sub>4</sub> were found at 21.586°, 27.691°, and 47.175°, which correspond to the facets (0 0 6), (1 0 2), and (1 1 0), respectively. The XRD pattern of the composite exhibits all the typical peaks of both ZnIn<sub>2</sub>S<sub>4</sub> and cobalt

tetraphenylporphyrin, indicating that the synthesis was effective.



**Fig. 1.** XRD patterns of (a) Porphyrin, (b) ZnIn<sub>2</sub>S<sub>4</sub>, (c) 25% porphyrin/ZnIn<sub>2</sub>S<sub>4</sub>, (d) JCPDS NO#65-2023 of ZnIn<sub>2</sub>S<sub>4</sub>

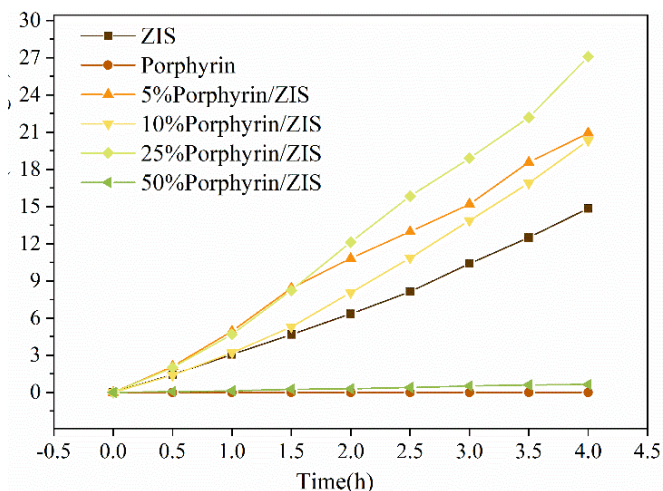
The photoluminescence spectrum (PL) in Fig. 3 demonstrates the performance of the photoexcited electrons and holes recombination. The intensity of the PL spectrum reflexes the recombination rate of the photogenerated pair: the lower the result of the PL spectrum, the greater the photocatalytic activity[16, 17]. ZnIn<sub>2</sub>S<sub>4</sub> monomer as shown exhibits an extremely high emission peak, indicating that the photogenerated carriers generated inside it have considerably recombined, whereas the emission peak intensity of cobalt tetraphenylporphyrin is at a low stage throughout the whole test range. The composite porphyrin/ZnIn<sub>2</sub>S<sub>4</sub> heterostructure has a lower peak intensity after the combination of cobalt tetraphenylporphyrin and ZnIn<sub>2</sub>S<sub>4</sub>.



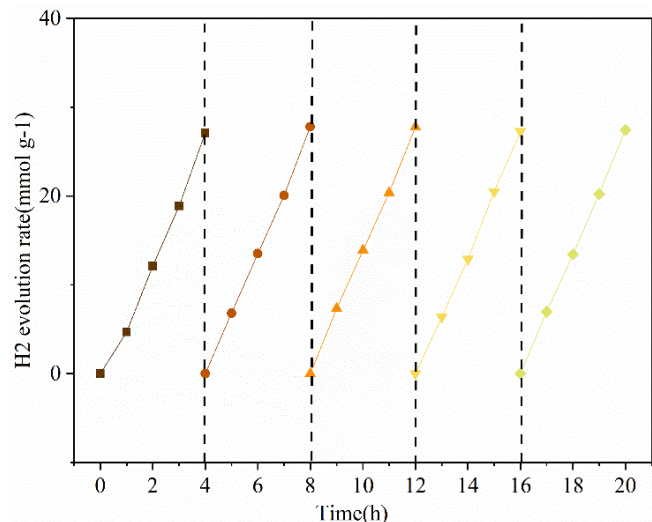
**Fig. 3.** Photoluminescence (PL) spectra of Porphyrin, ZnIn<sub>2</sub>S<sub>4</sub>, and 25% porphyrin/ZnIn<sub>2</sub>S<sub>4</sub>

It means that the heterojunction structure efficiently prevents the recombination of photocarriers in the system, hence enhancing the photocatalytic activity.

Under visible light (>420 nm) irradiation, the photocatalytic hydrogen generation performance of the material was investigated utilizing triethanolamine (TEOA) as a hole scavenger. The hydrogen gas evolution rate of each sample is illustrated in Fig. 6, where the hydrogen evolution rate of cobalt tetraphenylporphyrin is nearly undetectable and the H<sub>2</sub> evolution rate of ZnIn<sub>2</sub>S<sub>4</sub> is 3.8 mmol h<sup>-1</sup> g<sup>-1</sup>. When ZnIn<sub>2</sub>S<sub>4</sub> was coupled with cobalt tetraphenylporphyrin, the composite materials displayed significantly increased activity and reached a maximum of 6.9 mmol h<sup>-1</sup> g<sup>-1</sup> by the 25% porphyrin/ZnIn<sub>2</sub>S<sub>4</sub>, showing heterogeneous structure's effectiveness. Synthesized in a particular ratio, the structure has a positive effect on the improvement of photocatalytic activity. The rate of this H<sub>2</sub> generation is comparable to that described in prior publications, and the cost-effectiveness of the complex is attributed to the absence of noble metals in its synthesis. In Fig. 4, the 25% porphyrin/ZnIn<sub>2</sub>S<sub>4</sub> composite was also subjected to cycle testing, and the H<sub>2</sub> generation efficiency was robust in 5 batches of 20 h cycles. These results demonstrate that 25% porphyrin/ZnIn<sub>2</sub>S<sub>4</sub> is the most efficient and cost-effective heterostructure with enhanced photocatalytic hydrogen generation for water splitting.

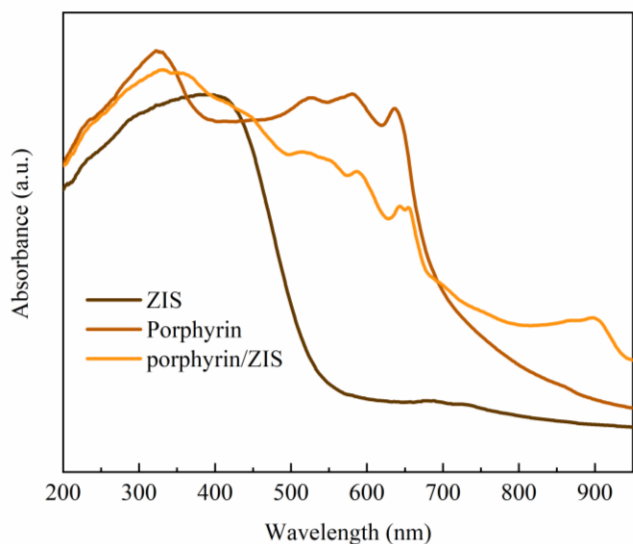


**Fig. 6.** H<sub>2</sub> generation rate with time by Porphyrin, ZnIn<sub>2</sub>S<sub>4</sub>, and different mass ratio of porphyrin/ZnIn<sub>2</sub>S<sub>4</sub> under visible light



**Fig. 4.** The recycle experiments of 25% porphyrin/ZnIn<sub>2</sub>S<sub>4</sub>

The UV-vis DRS spectrum from 200 to 900nm shown in Fig. 5 reflects the ability of each photocatalyst to absorb light in this wavelength range, in which the high light absorption ability is reflected by the increase in peak intensity [18]. The cobalt tetraphenylporphyrin exhibits strong absorption over the entire range, while ZnIn<sub>2</sub>S<sub>4</sub> has an absorption edge at about 550 nm. Compared with the two monomers, the 25% porphyrin/ZnIn<sub>2</sub>S<sub>4</sub> exhibited an improved absorbance intensity, especially after 650nm, which enables an improvement in the efficiency of photocatalytic hydrogen production.



**Fig. 5.** UV-vis DRS spectra of porphyrin, ZnIn<sub>2</sub>S<sub>4</sub>, and 25% porphyrin/ZnIn<sub>2</sub>S<sub>4</sub>

Tauc plots that can decide the band gap of each component by drawing the tangent line were shown in

Fig. 7. The Kubelka-Munk formula  $(ah\nu)^{1/n} = A(h\nu - E_g)$  was used to calculate the results [19, 20]. The band gap of  $ZnIn_2S_4$  and porphyrin was determined as 2.41 eV and 1.79 eV by this method, respectively.

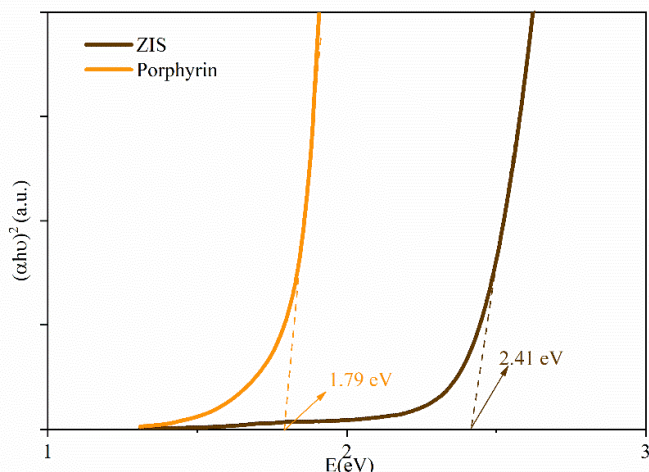


Fig. 7. Tauc plot of  $ZnIn_2S_4$  and porphyrin

The Mott-Schottky (MS) plot is used for determining the band positions of each component. Fig. 8 demonstrates that porphyrin and  $ZnIn_2S_4$  are both n-type semiconductors due to the positive slopes of their tangent lines. Thus, their CB positions can be calculated by their plot read  $E_{fb}$  minus 0.2V by convention, and the CB of porphyrin and  $ZnIn_2S_4$  are -1.69 eV and -1.09 eV (vs. NHE), respectively. Furthermore, the VB of porphyrin and  $ZnIn_2S_4$  can be calculated as 0.1 and 1.32 eV respectively by the formula:  $E_{VB} = E_{CB} + E_g$  and using the band gap got from above Fig. 5 results.

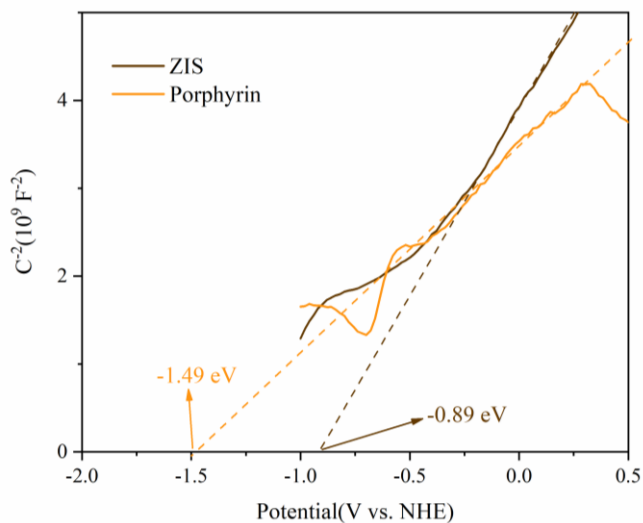


Fig. 8. Mott-Schottky plot of (a)  $ZnIn_2S_4$  and (b) porphyrin

As can be seen in Figure 9, in the band structure schematic illustration, the photoexcited electrons

efficiently travel across the strong interface between  $ZnIn_2S_4$  and cobalt tetraphenylporphyrin, from the conduction band of  $ZnIn_2S_4$  to the valence band of cobalt tetraphenylporphyrin, which serves to separate the hole and electron acceptor centers. Electrons emitted by cobalt tetraphenylporphyrin are caught by  $H^+$  in water, resulting in a reduction reaction that generates  $H_2$ . By transporting electrons from  $ZnIn_2S_4$  to cobalt tetraphenylporphyrin through an interface with long path, electron-hole pair recombination is decreased, and consequently enhancing photocatalytic activity[21, 22]. On the oxidized side, the sacrificial reagent quickly captures the holes created by  $ZnIn_2S_4$ . This Z-scheme heterostructure photocatalyst with a high hydrogen generation capacity and metal-free composition is a promising advancement for resolving energy issues through environmentally friendly and economy-effective photocatalysis.

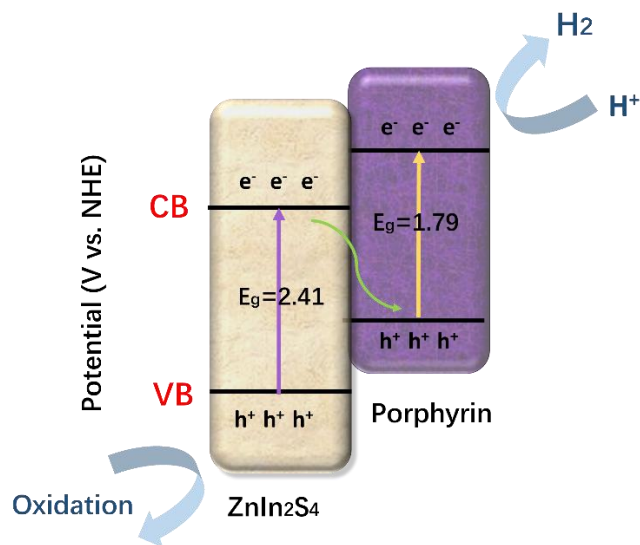


Fig. 9. Band structure schematic illustration of charge transfer mechanism of 25% porphyrin/ $ZnIn_2S_4$

### 2.3 Conclusions

An innovative Z-scheme heterostructure cobalt porphyrin/ $ZnIn_2S_4$  photocatalyst was created. This heterostructure enhances photocatalytic light absorption, carrier separation, and transport efficiency compared with monomers. Under visible light irradiation, the photocatalyst demonstrates a relatively high level of photocatalytic hydrogen evolution activity of  $6.9 \text{ mmol h}^{-1} \text{ g}^{-1}$ . Furtherly, because of the absence of noble metals, this discovery provides insight into the creation of heterostructure semiconductor photocatalysts that are highly efficient and cost-effective.

## ACKNOWLEDGEMENT

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## DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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