Cocatalyst designing: a binary noble-metal-free cocatalyst system consisting of ZnIn$_2$S$_4$ and In(OH)$_3$ for efficient visible-light photocatalytic water splitting

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A binary noble-metal-free cocatalyst consisting of ZnIn$_2$S$_4$ and In(OH)$_3$ was developed via a facile one-step hydrothermal method. The ZnIn$_2$S$_4$/In(OH)$_3$ modified ZnWO$_4$ nanocomposite exhibited enhanced photocatalytic H$_2$ evolution activity compared to all the related pure samples and binary composite photocatalysts under visible light irradiation. The enhanced photocatalytic hydrogen production activities can be attributed to the synergistic effects of the favorable light trapping ability and efficient spatial charge separation. The photocatalytic hydrogen evolution activity over other semiconductors, such as Zn$_2$SnO$_4$ and TiO$_2$, can also be significantly increased by loading ZnIn$_2$S$_4$/In(OH)$_3$ as a cocatalyst. The results clearly demonstrated that ZnIn$_2$S$_4$/In(OH)$_3$ is discovered as a new class of earth-abundant cocatalyst for water-splitting under visible light irradiation. It is expected that our work could provide a new strategy to improve the visible light response of semiconductors and facilitate their application in water splitting.

Introduction

Photocatalytic water-splitting is a promising approach for the clean, economical, and environmentally benign production of hydrogen by utilizing solar energy.$^{1-4}$ During the past few decades, many photocatalytic materials, such as sulfide-, oxide- and oxynitride based materials, have been extensively explored for hydrogen generation through splitting water.$^{5-11}$ However, none of them can meet the requirements for practical large-scale application to photocatalytic H$_2$ evolution under visible light. Hence, the highly efficient visible light photocatalysts for hydrogen production is still highly demanded for practical applications.

It is well-known that a cocatalyst plays a significant role in improving both the activity and stability of semiconductor photocatalysts. Noble metals such as Pt, Rh, Au and oxides such as RuO$_2$ are generally used as cocatalysts for photocatalytic hydrogen evolution. However, the above noble-metal based cocatalysts are too scarce and expensive. It is necessary to explore alternative cocatalysts based on inexpensive transition metals to facilitate the up-scaling of renewable H$_2$ production.

Recently, ZnIn$_2$S$_4$ with a suitable band gap (2.06–2.58 eV)$^{12,13}$ have been demonstrated to be excellent cocatalyst for CdIn$_2$S$_4$ and K$_2$La$_2$Ti$_3$O$_{10}$ in the photocatalytic hydrogen evolution.$^{14-16}$ It has been also proved to be an efficient visible-light driven photocatalyst or sensitizer to extend the absorption spectra of some wide-gap photocatalysts from the UV region to the visible region.$^{17,18}$

Furthermore, the unique 2D layer structure nanostructure of ZnIn$_2$S$_4$ enables its application as an excellent supporting matrix in the construction of heterostructured nanocomposite photocatalysts with high photocatalytic activity.$^{19-21}$ In addition, it was reported that indium ions can hydrolyze into In(OH)$_3$ when the pH value of the reaction system was above 2.5. So it is convenient to obtain ZnIn$_2$S$_4$/In(OH)$_3$ nanocomposite by a simple hydrothermal strategy by adjusting the pH value of the solution. In(OH)$_3$ is an important wide-gap semiconductor material with a direct bandgap of 5.15 eV.$^{22-25}$ The wide band gap provides photogenerated charge with stronger redox capability, favoring photocatalytic performance. Therefore it is expected that ZnIn$_2$S$_4$/In(OH)$_3$ can be an ideal candidate as a non-noble-metal cocatalyst system for water splitting under visible light irradiation.

Herein, the ZnIn$_2$S$_4$/In(OH)$_3$ modified ZnWO$_4$ nanocomposite was fabricated by a facile three-step hydrothermal strategy. The results revealed that as-prepared ternary ZnIn$_2$S$_4$/In(OH)$_3$/ZnWO$_4$ nanocomposite exhibited enhanced photocatalytic H$_2$-evolution activity than all the related pure samples.
and binary composite photocatalysts. Based on the experimental results, a possible synergistic mechanism for the enhanced photocatalytic H₂ evolution activity was proposed. The photocatalytic hydrogen evolution activity over other semiconductor such as Zn₂SnO₄ and TiO₂ can also be significantly increased by loading ZnIn₂S₄/In(OH)₃ as a cocatalyst. The results clearly demonstrated that ZnIn₂S₄/In(OH)₃ is discovered as a new class of earth-abundant cocatalyst for water-splitting under visible light irradiation. It is expected that our work could provide deep insight into design and application of new system with high activity for solar hydrogen generation in the future.

**Experimental**

**Preparation of photocatalysts**

**Synthesis of ZnIn₂S₄, In(OH)₃ and ZnIn₂S₄/In(OH)₃.** ZnIn₂S₄ was synthesized by a hydrothermal method. In a typical procedure, 0.300 g Zn(NO₃)₂-6H₂O, 0.782 g In(NO₃)₃-4.5H₂O and 0.616 g thiourea were dissolved in deionized water. The pH value of the solution was adjusted to 1.00 by adding 0.1 mol L⁻¹ HCl. The mixed solution was then transferred into a 100 mL Teflon-lined autoclave and heated at 180 °C for 12 h. After being cooled to room temperature, the yellow precipitate was collected by centrifugation and washed with ethanol and the distilled water for three times, respectively. And then it was dried at 80 °C to obtain the product.

The preparation of In(OH)₃ was similar to that of ZnIn₂S₄. In a typical procedure, 0.782 g In(NO₃)₃-4.5H₂O was added into the solution. The pH value of the solution was adjusted to 6 by adding 0.2 mol L⁻¹ NaOH. The mixed solution was then transferred into a 100 mL Teflon-lined autoclave and heated at 180 °C for 12 h. The remaining steps are the same as ZnIn₂S₄.

The synthesis of ZnIn₂S₄/In(OH)₃ is similar to that of ZnIn₂S₄. All of the experimental conditions are same except the initial pH value. The pH value of the solution was adjusted to 3.5, 4.5 and 5.5 with 0.2 mol L⁻¹ NaOH, respectively. The products synthesized at different pH values were labeled as ZnIn₂S₄/In(OH)₃-3.5, ZnIn₂S₄/In(OH)₃-4.5, ZnIn₂S₄/In(OH)₃-5.5, respectively.

**Preparation of ZnWO₄.** 5 mmol Na₃WO₄·2H₂O and 5 mmol Zn(NO₃)₂·6H₂O were added to 70 mL deionized water with magnetic stirring to form a homogeneous solution. The reaction mixture was then sealed in a 100 mL Teflon-sealed autoclave and maintained at 180 °C for 12 h. After being cooled to room temperature, the precipitate was collected by centrifugation and washed with ethanol and the distilled water for three times, respectively. Then it was dried at 80 °C to obtain the product.

**Photocatalytic H₂-production activity**

The photocatalytic hydrogen-production experiment was conducted in a closed gas circulation and evacuation system fitted with a top window Pyrex cell. A 300 W xenon lamp (PLS-SXE300C, Beijing Perfectlight Co. Ltd., China) which was positioned 10 cm away from the solution surface, coupled with a UV cut-off filter (λ > 420 nm) was used to provide the visible light. The focus intensity measured by a spectroradiometer (PM100D, Thorlabs, America) was 0.54 W cm⁻². In each run, 0.05 g photocatalyst was dispersed in a 100 mL aqueous solution containing 0.25 M Na₂SO₃ and 0.35 M Na₂S, which served as
a sacrificial agent. Before the irradiation with visible light, the suspension was degassed with N₂ for 1 h to drive away the O₂ in the system. The reaction cell was kept at room temperature with cooling water. The produced H₂ was detected using an online gas chromatography (GC7900, N₂ carrier, 5 Å molecular sieve column, TCD detector). The reaction was continued for 3 h. The apparent quantum efficiency (QE) was measured by the similar condition, but the light source was changed into high power LED (PLS-LED100B, Beijing Perfectlight Co. Ltd., China). The QE was calculated based on the following equation:

\[
\text{QE}(\%) = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% \\
= \frac{2 \times \text{number of evolved } H_2 \text{ molecules}}{\text{number of incident photons}} \times 100\%
\]

**Photoelectrochemical measurements**

The working electrodes were prepared as follows: 0.05 g of the sample, 0.05 g of polyethylene glycol (molecular weight 20 000) and 0.5 mL of ethanol were mixed and ground into the slurry. Then the slurry was evenly coated onto a 2 cm × 1.2 cm F-doped SnO₂-coated (FTO) glass electrode by the doctor blade method. The area and the thickness of the coating layer were limited to 1 cm² and 0.01 mm, respectively. Finally, the prepared electrodes were dried in an oven at 100 °C for 60 min. The measurement of the photocurrent and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical analyzer (CHI660E, Shanghai Chenhua Limited, China) in a standard three-electrode system. In this system, the prepared glass electrodes were used as the working electrodes. Pt wire and Ag/AgCl (saturated 0.3 M KCl) were used as counter electrode and reference electrode, respectively. The three electrodes were connected by the electrolyte of 0.5 M Na₂SO₄. The source of visible light is a 300 W Xe lamp with a UV cut-off filter (λ > 420 nm). The EIS were tested in the same standard three-electrode system. In this system, the phase frequency and amplitude-frequency characteristics were recorded over frequency range from 0.01 Hz to 10⁵ Hz, and then the spectrum was transferred into Nyquist diagram.

**Results and discussion**

**Structure and properties characterization**

Fig. 1 shows X-ray diffraction (XRD) patterns of as-prepared samples. The results show that the diffraction peaks of the pure ZnIn₂S₄, pure In(OH)₃, and pure ZnWO₄ sample are in good agreement with the hexagonal phase of ZnIn₂S₄ (JCPDS card No. 03-065-2023), the cubic phase of In(OH)₃ (JCPDS card No. 76-1464) and monoclinic structure of ZnWO₄ (JCPDS card No. 73-0554), respectively. For the as-prepared ternary ZIZ composites, all the ZnIn₂S₄ and ZnWO₄ diffraction peaks were found. The characteristic peaks of In(OH)₃ (22.3°, 31.7° and 51.2°) can also be found. When the pH increases during the synthesis of ZnIn₂S₄/In(OH)₃, the characteristic peak of ZnIn₂S₄ at 21.4° becomes weaker, while the peak of In(OH)₃, at 22.3°, 31.7° and 51.2° become stronger. This demonstrates that the increasing pH value can improve the growth of In(OH)₃. No traces of other phases were detected, indicating the high purity of the samples and confirming that ZnIn₂S₄/In(OH)₃ and ZnWO₄ coupled together successfully and without other phases.

The morphology of the samples was investigated by SEM. Fig. 2a shows the SEM image of the as-prepared ZnIn₂S₄ at a higher magnification. It is shown that the ZnIn₂S₄ microsphere has a unique marigold-like spherical superstructure composed of numerous nanosheets. As shown in Fig. 2b, the as-prepared pure In(OH)₃ was made up of rectangular blocks with an edge of about 0.7–2 μm. It is also clearly seen that some small nanoparticles are attached to the edge of rectangular blocks, indicating that In(OH)₃ rectangular blocks may be formed by the adsorption of small In(OH)₃ nanoparticles via an Oswald ripening mechanism. As shown in Fig. 2c, the as-prepared ZnWO₄ was composed of nanoparticles with a wide size distribution. Fig. 2d and e show the SEM image of the ZIZ-4.5 nanocomposite. It is clearly observed that In(OH)₃ cubic blocks and ZnWO₄ nanoparticles were attached to the surface of ZnIn₂S₄ microspheres. Fig. 2f shows the HRTEM images of as-prepared ZIZ-4.5 sample. As shown in Fig. 2f, the fringes of 0.33 nm, 0.29 nm and 0.48 nm correspond to the (102), (220) and (100) plane of ZnIn₂S₄, In(OH)₃ and ZnWO₄, respectively. The EDS spectrum (Fig. 3) of the composite clearly confirms the presence of Zn, In, S, O and W elements. From the above results, it can be seen that ZIZ composites with close contact have been successfully fabricated.

To characterize the chemical composition of as-prepared ZIZ photocatalyst, X-ray photoelectron spectroscopy (XPS) measurement was used to determine the exact surface state. The XPS survey spectrum confirms that the composite is mainly composed of Zn, In, S, W and O (Fig. 4a). The high-resolution XPS spectra of Zn 2p region of the catalyst was shown in Fig. 4b. The XPS signals of Zn 2p were observed at binding energies at around 1021.9 eV (Zn 2p₁/₂) and 1044.9 eV (Zn 2p₃/₂). The high resolution XPS spectra of In 3d region of the catalyst was shown in Fig. 4c. The XPS signals of In 3d were observed at binding energies at around 445.0 eV (In 3d₅/₂) and 452.6 eV (In 3d₃/₂), which are in good agreement with the previous works. As illustrated in Fig. 4d, the appearance of S 2p₃/₂ and S 2p₁/₂...
peaks at 161.9 and 163.0 eV can be assigned to the S$^{2-}$ in ZnIn$_2$S$_4$\cite{33}. The XPS spectrum in the W 4f region exhibits binding energy at 35.8 eV for W 4f$_{7/2}$ and 37.9 eV for W 4f$_{5/2}$ (Fig. 4e), the gap between them is about 2.1 eV, which is close to the value of reference\cite{34}, indicating that the W element exhibits in the chemical formation of W$^{6+}$. The O 1s region can be fitted by three peaks with binding energies of 530.5 eV, 531.5 eV, and 533.5 eV. The peaks at 530.5 eV and 531.5 eV correspond to the lattice oxygen in ZnWO$_4$ and In(OH)$_3$\cite{35,36} respectively. While the peaks at 533.5 eV can be attributed to the oxygen in the adsorbed H$_2$O on the surface of sample. The above results show that the prepared sample is ZIZ.

The nitrogen adsorption–desorption isotherms of ZIZ-4.5, ZnIn$_2$S$_4$, In(OH)$_3$, and ZnWO$_4$ are shown in Fig. 5. The obtained results from the sorption isotherms suggest that all samples exhibit a type IV isotherm with a H3 hysteresis loop according to the IUPAC standard\cite{30,36,37}, indicating the existence of a mesoporous structure or slit-like pore. The porous structure parameters of pure ZnIn$_2$S$_4$, In(OH)$_3$, ZnWO$_4$ and ZIZ-4.5 composites are listed in Table 1. The BET surface area ($S_{BET}$) of the pure ZnIn$_2$S$_4$, In(OH)$_3$, ZnWO$_4$ was 33.730, 13.736, and 11.876 m$^2$ g$^{-1}$, respectively. The BET surface area of the ZIZ-4.5 nanocomposite was 27.274 m$^2$ g$^{-1}$, which is lower than that of ZnIn$_2$S$_4$. The reduction of $S_{BET}$ in the ternary sample may be ascribed to the blockage of partial macropores due to the

Fig. 2  SEM images of (a) ZnIn$_2$S$_4$, (b) In(OH)$_3$, (c) ZnWO$_4$, (d and e) ZIZ-4.5, (f) HRTEM images of ZIZ-4.5.

Fig. 3  EDS spectrum of ZIZ-4.5 sample.

Fig. 4  XPS spectra of the ZIZ-4.5 sample: (a) survey, (b) Zn 2p, (c) In 3d, (d) S 2p, (e) W 4f and (f) O 1s.
ZnIn₂S₄, In(OH)₃, and ZnWO₄ are very close to previously reported results.⁴²–⁴⁴

The valence band edge potential and the conduction band edge potential of a semiconductor material can be determined by using the following equation:⁴⁵,⁴⁶

\[ E_{VB} = X - E^g + 0.5E_g \]  

\[ E_{CB} = E_{VB} - E_g \]  

where \( E_{VB} \) represents valence band edge potential, \( X \) is the electronegativity of the semiconductor estimated by the geometric mean of the electronegativity of the constituent atoms, \( E^g \) is the energy of free electrons on the hydrogen scale (4.5 eV), \( E_g \) is the band gap energy of the semiconductor, \( E_{CB} \) is the conduction band edge potential. The \( X \) value of pure ZnIn₂S₄, In(OH)₃ and ZnWO₄ is about 4.82, 6.155 and 5.55 eV,⁴⁴,⁴⁶ respectively. The \( E_{VB} \) of bare ZnIn₂S₄, In(OH)₃ and ZnWO₄ can be assigned to be +1.57, +4.15 and +2.97 eV, respectively. The corresponding \( E_{CB} \) of ZnIn₂S₄, In(OH)₃ and ZnWO₄ can be estimated to be −0.93, −0.84 and −0.87 eV, respectively.

**Photocatalytic activities**

Photocatalytic H₂ production experiments were carried out over these as-prepared photocatalysts in the presence of Na₂SO₃ and Na₂S as the sacrificial reagents under visible light irradiation (\( \lambda > 420 \text{ nm} \)).⁴⁸ As shown in Fig. 6, pure ZnWO₄ (116.7 μmol g⁻¹ h⁻¹), pure In(OH)₃ (13.4 μmol g⁻¹ h⁻¹) and pure ZnIn₂S₄ (187.6 μmol g⁻¹ h⁻¹) show their low photocatalytic activity, respectively. The ternary ZnIn₂S₄/In(OH)₃/ZnWO₄ (ZIZ) nanocomposite exhibited enhanced photocatalytic H₂ evolution activity as compared to all the related pure samples and binary composite photocatalysts. Especially, ZIZ-4.5 shows the highest photocatalytic activity with a H₂ evolution rate of 1030.1 μmol g⁻¹ h⁻¹, which was 8.83 times higher than that of ZnWO₄ alone. Moreover, the apparent quantum efficiency (QE) for H₂ evolution was examined at 420 nm to further evaluate the photocatalytic activity of ZIZ-4.5. The corresponding QE reached 8.1%, which indicated that the ZIZ-4.5 is a highly-efficient photocatalyst.

**Table 1** The BJH pore size, surface areas, pore volumes of the photocatalytic materials

|       | ZnIn₂S₄ | In(OH)₃ | ZnWO₄ | ZIZ-4.5 |
|-------|---------|---------|-------|---------|
| BJH pore size (nm) | 3.849 | 17.500 | 18.063 | 3.329 |
| BET surface area (m² g⁻¹) | 33.730 | 13.736 | 11.876 | 27.274 |
| Pore volume (cm³ g⁻¹) | 0.205 | 0.142 | 0.109 | 0.123 |

The surface covering of In(OH)₃ rectangular blocks and ZnWO₄ nanoparticles on the bare ZnIn₂S₄.

The optical absorption properties of as-prepared samples were evaluated by UV-vis diffuse reflection spectra (DRS) measurement (Fig. S1a†). The pristine ZnWO₄ showed a narrowed light absorption edge of no more than 380 nm, due to its intrinsic wide band gap.³⁸ The pure In(OH)₃ has weak absorption ability with an absorption edge of ca. 250 nm.²⁴ The pure ZnIn₂S₄ has a strong absorption in the wavelength ranging from 200 to 550 nm.³⁹ The introduction of ZnIn₂S₄ increases the light absorption of composite materials in the range of the visible light region. ZIZ-4.5 composite has a strong absorption both in the UV region and visible light region (Fig. S1a†).

The energy level and band gap of the semiconductors play a crucial role in determining their physical properties. The band gap energy of a semiconductor can be calculated by the following formula:

\[ \alpha hν = A(hν - E_g)^{n/2} \]  

where \( \alpha \), \( h \), \( ν \), \( E_g \) and \( A \) are the absorption coefficient, Planck constant, light frequency, band gap energy, and a constant, respectively. Among them, \( n \) is determined from the type of optical transition of a semiconductor (\( n = 1 \) for direct transition and \( n = 4 \) for indirect transition). The \( n \) value of ZnIn₂S₄, In(OH)₃, and ZnWO₄ is 1 for the direct transition.³⁰,³¹ Therefore, the band gap energy (\( E_g \) value) of the samples can be estimated from a plot of \( \alpha hν^2 \) vs. \( hν \). The band gap energy of ZnIn₂S₄, In(OH)₃, and ZnWO₄ is 2.50 eV, 4.99 eV and 3.84 eV, respectively (Fig. S1b†). All the values for the band gap of ZnIn₂S₄, In(OH)₃, and ZnWO₄ are very close to previously reported results.³²–³⁴
photocatalyst for hydrogen evolution under visible light irradiation. A further increase of pH value will lead to a significant reduction of the photocatalytic H2-evolution rate. With increasing pH value, more ZnIn2S4 transformed into In(OH)3 through the hydrolysis reaction of In3+ ions, which is evidenced from the XRD measurements (Fig. 1e–g). Excessive amount of In(OH)3 particles may cover the active sites on the surface of composite, shield the incident light and act as charge recombination centers. In addition, the decrease of ZnIn2S4 can result in the reduction of the utilization of visible light, leading to the decrease of hydrogen production activity.

To confirm the stability of our composite catalysts, we performed four consecutive hydrogen evolution runs over ZIZ-4.5 under the same conditions (Fig. S2†). Each cycle was performed under visible light irradiation for 3 h. After each run, the reaction system was re-evacuated. The H2 evolution rate after the fourth cycle can keep ca. 91% of the initial rate. This decrease of the H2 evolution rate from 3090 to 2805 μmol g−1 after four cycles could be attributed to the continuous consumption of Na2S and Na2SO3. The above results indicate that the prepared ZIZ-4.5 composite has good stability during photocatalytic reactions.

Possible mechanism of photocatalytic H2 evolution

A schematic illustration of the tentative mechanism proposed for the high H2 production activity of the ternary ZIZ composite is shown in Fig. 7. Under visible light illumination, ZnIn2S4 with narrow bandgap energy (2.50 eV in this work) can be easily excited and generate electrons and holes. Normally, these photogenerated electrons and holes recombine rapidly, resulting in a poor H2 evolution activity of pure ZnIn2S4. However, in the ternary ZIZ composite system, since the CB of ZnIn2S4 (−0.93 eV) is more negative than that of In(OH)3 (−0.84 eV) and ZnWO4 (−0.87 eV), the photogenerated electrons in the CB of ZnIn2S4 can be transferred to the CB of In(OH)3 and ZnWO4 (Fig. 7), where the electrons can effectively reduce H+ and produce H2 molecules. Meanwhile, holes accumulated at the VB of ZnIn2S4 could be consumed by the sacrificial agent (S2−, SO32−). Owning to the close contact of ZIZ composite, photogenerated electron can be transferred quickly, so as to extend the charge carriers lifetime and reduce the recombination of electron–hole pairs. Consequently, the high photocatalytic H2-production activity is achieved over the ternary ZIZ composite.

The charge recombination and transfer can be investigated by photoluminescence (PL) spectra. It can also help understanding the fate of photogenerated electrons and holes in semiconductor because PL emission results from the recombination of free carriers. The PL spectra of ZIZ-4.5, ZnIn2S4, In(OH)3 and ZnWO4 samples were recorded at room temperature with an excitation wavelength of 215 nm (Fig. S3†). It can be observed that the bare ZnIn2S4 shows a strong peak at about 550 nm, which can be attributed to the direct recombination of the photo-generated electron–hole pairs in ZnIn2S4 nanocrystals. When introducing both ZnWO4 and an optimum concentration of In(OH)3 content, ZIZ nanocomposite exhibited much lower PL emission peak at about 470 nm. The results implied that ZIZ has remarkably enhanced separation efficiency of photo-induced electron–hole pairs, which is qualitatively in good agreement with the trend in photo-activity enhancement.

To further deeply understand the photocatalytic enhancement mechanism for H2 evolution, the transfer and separation of photo-generated charge carriers were also investigated through the photoelectrochemical (PEC) analysis. The transient
photocurrent responses of ZnIn$_2$S$_4$, In(OH)$_3$, ZnWO$_4$ and ZIZ-4.5 with typical on–off cycles of intermittent irradiation were measured (Fig. S4a†). Notably, the photocurrent of ZIZ-4.5 sample is much higher than the other samples, confirming the more efficient interfacial mobility and separation of photo-generated electron–hole pairs for the ZIZ-4.5 composite sample. In addition, the electrochemical impedance spectroscopy (EIS) has also been investigated to provide sufficient evidence for the interfacial charge transfer resistance and separation efficiency. The electrochemical impedance spectroscopy (EIS) of these four samples were shown (Fig. S4b†). It is observed that the arc radius in the Nyquist plots of ZIZ-4.5 is much smaller than those samples were shown (Fig. S4b†). Notably, the photocurrent of ZIZ-4.5 with typical on–off cycles of intermittent irradiation was much higher than the other samples, confirming that introducing ZnIn$_2$S$_4$/In(OH)$_3$ system is an effective way to improve the photocatalytic efficiency of ZnWO$_4$.

Although the results here obtained certainly open up the possibility to design a noble-metal-free photocatalyst for water splitting, the deposition of the ZnIn$_2$S$_4$/In(OH)$_3$ cocatalyst on other semiconductor is certainly required. As shown in Fig. 8, the photocatalytic H$_2$-production activity of Zn$_2$SnO$_4$ and TiO$_2$ were both tremendously improved by loading the specified amount of ZnIn$_2$S$_4$/In(OH)$_3$ as cocatalyst. It is expected that the combination of ZnIn$_2$S$_4$ and In(OH)$_3$ as a new class of earth-abundant cocatalyst can become a general strategy to improve the H$_2$-evolution activity over various kinds of conventional semiconductors.

**Conclusions**

In conclusion, the combination of ZnIn$_2$S$_4$ with In(OH)$_3$, formed a new class of earth-abundant cocatalyst for water-splitting under visible light irradiation, which greatly advanced the photocatalytic activity of ZnWO$_4$ promoted by synergetic effects. The roles of ZnIn$_2$S$_4$ and In(OH)$_3$, in boosting the H$_2$ evolution activity of ZnWO$_4$ were revealed. This work could not only provide an excellent candidate for visible-light H$_2$ evolution, but also opens new possibilities to provide insight into the design of new system with high activity for solar hydrogen generation.

**Conflicts of interest**

There are no conflicts to declare.

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