Research Article

Highly Efficient Photocatalytic Hydrogen on CoS/TiO₂ Photocatalysts from Aqueous Methanol Solution

Yu Niu ¹, Fuying Li ¹, Kai Yang,² Qiyou Wu,¹ Peijing Xu,¹ and Renzhang Wang¹

¹Fujian Provincial Collaborative Innovation Center for Clean Coal Gasification, Technology College of Resources and Chemical Engineering, Sanming University, Sanming 365004, China

²School of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

Correspondence should be addressed to Yu Niu; niuyu200704@163.com

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The photocatalyzed water splitting reaction in aqueous methanol solution is an efficient preparation method for hydrogen and methanol under mild conditions. In this work, metal sulfide-loaded TiO₂ photocatalysts for hydrogen and methanol production were synthesized by hydrothermal method (180°C/12 h) and characterized by X-ray diffraction (XRD), UV-visible diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). The crystal structures of the samples are the typical anatase phase of TiO₂ and exhibit a spherical morphology. When TiO₂ was loaded with CoS, ZnS, and Bi₂S₃, respectively, the resulting catalysts showed photocatalytic activities for water decomposition to hydrogen in aqueous methanol solution under 300 W Xe lamp irradiation. Among the photocatalysts with various compositions, the 20 wt% CoS/TiO₂ sample with a 2.1 eV band gap showed the maximum photocatalytic activity for the photocatalytic reaction, which indicated that CoS improved the separation ratio of photoexcited electrons and holes. The enhanced activity can be attributed to the intimate junctions that are formed between CoS and TiO₂, which can reduce the electron-hole recombination. The production rate of hydrogen with 20 wt% CoS/TiO₂ photocatalyst was about 5.6 mmol/g/h, which was 67 times higher than that of pure TiO₂. The formation rate of HCHO was 1.9 mmol/g/h with 98.7% selectivity. Moreover, the CoS/TiO₂ photocatalyst demonstrated good reusability and stability. In the present study, it is demonstrated that CoS can act as an effective cocatalyst to enhance the photocatalytic hydrogen and methanol production activity of TiO₂. The highly improved performance of the CoS/TiO₂ composite was mainly ascribed to the efficient charge separation.

1. Introduction

Photocatalytic water splitting into hydrogen, a renewable, clean-burning, and environmental-friendly fuel for future energy sources, is considered as one of the most significant and attractive solutions to solve the global energy and environmental problems [1–3]. A previous study found that adding methanol (CH₃OH) to pure water can dramatically enhance H₂ production, suggesting that CH₃OH plays a crucial role in H₂ production [4]. Methanol is used as a raw material for the industrial production of methanol through an oxidation reaction using Ag, Cu, or V₂O₅ as catalysts. However, this process requires high temperatures of 700–900 K and expensive catalysts. Photocatalytic production of

both hydrogen and methanol from aqueous methanol solution using photocatalysts is an efficient approach to address the above problems. Moreover, the photocatalytic reaction conditions are mild compared to industrial methods. Fujishima and Honda first observed the splitting of water at a TiO₂ electrode under the irradiation of ultraviolet (UV) light in 1972 [5]. Since then, TiO₂ is considered one of the most promising semiconductor photocatalysts due to its superior photo reactivity, nontoxicity, long-term stability, and low cost [1, 6]. TiO₂ has also received a lot of attention as a photocatalyst for hydrogen production [7, 8]. However, the photocatalytic decomposition of water on pure TiO₂ photocatalyst is ineffective. One reason is that the production of hydrogen is limited by the rapid recombination of

photoexcited holes and electrons. To improve the photocatalytic efficiency, one of the effective strategies is to develop cocatalyst-modified photocatalysts [9–13]. According to previous research, CdS photocatalysts facilitate the production of H_2 by promoting the separation of photoexcited electrons and holes [14–16]. However, CdS is noxious, environmentally hazardous, and costly [17]. Therefore, developing suitable photocatalysts for H_2 production is important and extremely urgent. Our research is focused on the development of nontoxic, environmentally friendly, and inexpensive promoters, such as CoS, ZnS, and Bi_2S_3 . Although metal sulfides have demonstrated high activity in H_2 involving reactions in heterogeneous catalysis, CoS has rarely been used as a cocatalyst in photocatalytic H_2 production. In our research, different photocatalysts were successfully prepared through the hydrothermal method and were characterized using XRD, UV-visible DRS, SEM, and EDX analyses. CoS, ZnS, and Bi_2S_3 were investigated as cocatalysts for photocatalytic H_2 and methanol production from methanol solution under 300 W Xe lamp irradiation. The stability and reusability of the catalyst were also evaluated.

2. Experimental

2.1. Catalyst Preparation. All the chemicals were of reagent grade and used as received without any further purification.

The metal sulfide samples were prepared by the hydrothermal method [18]. In a typical procedure, 5 mL deionized water and 20 mL ethyl alcohol were stirred at room temperature for 0.5 h. Different metal salts ($Co(NO_3)_3 \cdot 6H_2O$, 1.46 g; $Zn(CH_3COO)_2$, 0.92 g; $Bi(NO_3)_3 \cdot 5H_2O$, 1.62 g) and thiourea ($(NH_4)_2S$, 0.38 g), which were used as the Co, Zn, Bi, and S precursors, were added to the above solution. The mixture was continuously stirred for 0.5 h and ultrasonicated for 0.5 h to obtain a well-mixed solution. The mixture was then transferred to a Teflon-lined autoclave and heated at $180^\circ C$ for 12 h. The resulting precipitate was collected by centrifugation and washed successively with distilled water and ethanol three times to remove unbound impurities. It was then dried at $60^\circ C$ in air for 12 h and ground for 1 h.

The metal sulfide-loaded TiO_2 samples were prepared by the hydrothermal method [19]. In a typical procedure, different amounts of CoS powder were dissolved in 1 mL tetrabutyl titanate and 5 mL ethyl alcohol, and the mixture was stirred at room temperature for 0.5 h. Then, 20 mL deionized water and ammonia water (to adjust $pH=10$) were added to the above solution. The solution was continuously stirred for 0.5 h and ultrasonicated for 0.5 h to achieve a well-mixed solution. The mixture was then transferred to a Teflon-lined autoclave and heated at $180^\circ C$ for 12 h. The resulting precipitate was collected by centrifugation and washed successively with distilled water and ethanol three times to remove unbound impurities. The product was then dried at $60^\circ C$ in air for 12 h and ground for 1 h and labeled as CoS/TiO_2 .

The procedure for the preparation of TiO_2 , ZnS/TiO_2 , and Bi_2S_3/TiO_2 was the same as that for CoS/TiO_2 , except for the different precursors.

FIGURE 1: XRD patterns of CoS/TiO_2 , ZnS/TiO_2 , and Bi_2S_3/TiO_2 .

2.2. Characterization of Catalysts. The phase compositions of the samples were determined from their XRD patterns, which were obtained using an X'Pert X-ray diffractometer (PANalytical, Netherlands) using $Cu K\alpha$ radiation ($\lambda = 0.15406 nm$) at a scan rate of $2^\circ/min$ from 20° to 80° (2θ). The accelerating voltage and applied current were 40 kV and 30 mA, respectively [20].

The micro structures of the samples were determined using SEM images obtained at an accelerating voltage of 20 kV using a ZEISS SIGMA instrument.

The UV-vis diffuse reflection spectra (DRS) were recorded using a Varian Cary 500 Scan UV-vis-NIR spectrometer with $BaSO_4$ as the reference sample. The reflectance spectra were transformed into absorption intensity by using Kubelka-Munk method.

2.3. Catalytic Performance. The photocatalytic reactions were carried out in a sealed quartz tube reactor (volume, 25 mL). The light source was a 300 W Xe lamp. The solid catalyst powder (25 mg) was ultrasonically dispersed in 5.0 mL of mixed solution containing 76 wt% CH_3OH and 24 wt% H_2O . Then, the reactor was evacuated and filled with high-purity (99.999%) nitrogen. The photocatalytic reaction was carried out at room temperature for 12 h. After the reaction, the liquid products were analyzed by high-performance liquid chromatography (HPLC, Shimadzu LC-20A) with both refractive index and UV detectors. The stationary phase was a Shodex SUGARSH-1011 column ($8 \times 300 mm$) and the mobile phase was a dilute H_2SO_4 aqueous solution. H_2 contents were analyzed by an Agilent Micro GC3000 equipped with a molecular sieve 5A column and a high-sensitivity thermal conductivity detector [21].

3. Results and Discussion

3.1. Characterization of the Samples. The crystalline phases of the samples were characterized by their XRD patterns. Figure 1 shows the XRD patterns of CoS/TiO_2 , ZnS/TiO_2 , and Bi_2S_3/TiO_2 nanoparticles. For all the samples, the peaks at $2\theta = 25.1^\circ$, 37.6° , 48.0° , 53.8° , 55.0° , and 62.7° can be attributed to the typical anatase phase of TiO_2 (JCPDS: 21-1272) [22]. The XRD patterns show that the loading of metal sulfide nanoparticles did not change the crystal structure of TiO_2 . The peaks at $2\theta = 28.7^\circ$ and 29.9° with low intensity can be

attributed to CoS [23]. The peak at $2\theta = 28.6^\circ$ with a low intensity is due to ZnS [24]. The peaks at $2\theta = 28.0^\circ$, 29.3° , and 32.5° with low intensity can be attributed to Bi_2S_3 [25].

3.2. UV-Vis Diffuse Reflection Spectra (DRS). Figure 2 shows the DRS of TiO_2 , CoS/TiO_2 , ZnS/TiO_2 , and $\text{Bi}_2\text{S}_3/\text{TiO}_2$ samples. It can be observed from the spectra that the metal sulfide-loaded TiO_2 samples have enhanced absorption in the visible-light region compared to pure TiO_2 . Specifically, CoS/TiO_2 showed stronger absorption than ZnS/TiO_2 and $\text{Bi}_2\text{S}_3/\text{TiO}_2$. Compared to pure TiO_2 and metal sulfide-loaded TiO_2 , the broader absorption bands can be attributed to the type of loaded metal sulfide nanoparticles. The $(ah\nu)^{1/2}$ vs $(h\nu)$ spectra were obtained from the corresponding diffuse reflectance spectra by means of the Kubelka-Munk function [26]. Figure 3 shows the curves of $(ah\nu)^{1/2}$ vs $(h\nu)$ for the samples. By extrapolating the linear portion of the curves to $(ah\nu)^{1/2} = 0$, the E_g values of TiO_2 , CoS/TiO_2 , ZnS/TiO_2 , and $\text{Bi}_2\text{S}_3/\text{TiO}_2$ were determined to be 3.4 eV, 2.1 eV, 3.2 eV, and 2.4 eV, respectively. As a result, CoS/TiO_2 has the largest visible light absorption capacity and the smallest band gap energy. This result is consistent with the fact that the increase in wavelength range of absorption edge in semiconductors is related to the decrease in optical absorption edge energy.

3.3. Morphologies of Samples. SEM and EDX analyses of the samples were carried out to determine the morphologies, polycrystalline structure, and elemental composition of the samples. The SEM images of 20 wt% CoS/TiO_2 , 40 wt% CoS/TiO_2 , and 60 wt% CoS/TiO_2 samples are presented in Figures 4(a)–4(c), respectively. It can be seen in Figure 4(a) that most of the crystallites are spherical, and their morphologies are almost the same. It can be seen in Figures 4(b) and 4(c) that the crystallite shape transforms from particles to platelets with increase in content of CoS. The SEM images indicate that 20 wt% CoS/TiO_2 nanoparticles showed the best dispersion among all the samples. The EDX spectrum in Figure 4(d) for 20 wt% CoS/TiO_2 sample shows the signals of Ti, O, Co, and S elements.

3.4. Photocatalytic Performance of Samples. The photocatalytic activities of TiO_2 , CoS/TiO_2 , ZnS/TiO_2 , and $\text{Bi}_2\text{S}_3/\text{TiO}_2$ samples were evaluated using the photocatalytic hydrogen generation reaction in aqueous methanol solution. The results are shown in Figure 5. As can be seen from the figure, the loaded metal sulfides have a significant influence on the photocatalytic activity of TiO_2 . When there was no metal sulfide, pure TiO_2 showed low photocatalytic activity because of the rapid recombination between Conduction Band (CB) electrons and Valence Band (VB) holes [27]. Moreover, we found that CoS is a better cocatalyst for H_2 production than ZnS and Bi_2S_3 . The photocatalytic activity of the samples decreased in the following order: $\text{CoS}/\text{TiO}_2 > \text{Bi}_2\text{S}_3/\text{TiO}_2 > \text{ZnS}/\text{TiO}_2 > \text{TiO}_2$. In the liquid phase reaction, HCHO was the major product along with H_2 .

Figure 6 shows a comparison of the photocatalytic H_2 production activities of the 5 wt%, 10 wt%, 20 wt%, 40 wt%, and 60 wt% CoS/TiO_2 samples in aqueous methanol

FIGURE 2: UV-vis DRS of the samples.

FIGURE 3: Plots of $(ah\nu)^{1/2}$ vs $(h\nu)$ for estimating optical band gaps of the samples.

solution. As can be seen from the figure, the content of CoS has a significant influence on the photocatalytic activity of TiO_2 . The photocatalytic activity of the samples increased as the content of CoS increased from 5% to 20%. The highest hydrogen and methanol production rates were obtained for the 20 wt% CoS/TiO_2 sample. The H_2 formation rate was 5.6 mmol/g/h, which is 67 times higher than that of pure TiO_2 . The formation rate of HCHO was 1.9 mmol/g/h with 98.7% selectivity. As shown in Figure 6, further increase in CoS content resulted in reduced photocatalytic activity. Based on the Debye-Scherrer equation, the calculated crystalline lattice sizes are summarized in Table 1. It is clear that the lattice size increased with the content of the CoS composite, indicating that the introduction of CoS can accelerate the aggregation and growth of TiO_2 nanocrystals. As a result, although an appropriate CoS content plays a role in increasing the photocatalytic activity, the larger TiO_2 nanocrystals lead to decreased photocatalytic activity. Moreover, we speculate that the reaction mechanism involves the activation of C–H bond and O–H bond in methanol by photoexcited holes on CoS/TiO_2 surface. The photogenerated electrons will transfer to the surface of CoS/TiO_2 and reduce protons to H_2 .

The capability for reuse is one of the most important factors for an ideal photocatalyst. Hence, the reusability and stability of the 20 wt% CoS/TiO_2 sample were investigated. The sample was collected after each photocatalytic H_2 production experiment and reused for five times. Figure 7 shows

FIGURE 4: (a) SEM image of 20 wt% CoS/TiO₂, (b) SEM image of 40 wt% CoS/TiO₂, (c) SEM image of 60 wt% CoS/TiO₂, and (d) EDX spectrum of 20 wt% CoS/TiO₂.

FIGURE 5: Photocatalytic H₂ production activity of the samples.

FIGURE 6: Photocatalytic H₂ production activity of CoS/TiO₂.

the results of five successive H₂ production runs under the same experimental conditions. It can be seen that 20 wt% CoS/TiO₂ does not exhibit a significant loss in photocatalytic activity in the five recycles.

TABLE 1: Lattice size of CoS/TiO₂.

Sample	FWHM (rad)	2Theta (°)	Lattice size (nm)
5 wt% CoS/TiO ₂	0.90	25.24	8.85
10 wt% CoS/TiO ₂	0.88	25.24	9.37
20 wt% CoS/TiO ₂	0.87	25.24	9.98
40 wt% CoS/TiO ₂	0.55	25.24	15.79
60 wt% CoS/TiO ₂	0.51	25.25	17.03

FIGURE 7: Recycling of 20 wt% CoS/TiO₂ for photocatalytic H₂ production.

3.5. Reaction Mechanism. A possible mechanism for the H₂ and HCHO production over the CoS/TiO₂ photocatalyst proposed is shown in Figure 8. Obviously, the CoS/TiO₂ sample as an oxidation and reduction semiconductor can be excited under simulated solar light irradiation. Subsequently, the photogenerated holes will migrate to the host photocatalyst surface, react with methanol, and drive the

FIGURE 8: Schematic diagram of charge transfer process.

generation of HCHO. Photogenerated electrons in the CB of TiO_2 could quickly transfer to CoS and recombine with holes in the VB of CoS. Then, the electrons in the CB of CoS with stronger reduction ability could drive the generation of H_2 . Clearly, TiO_2 lacks the active sites for H_2 evolution, so the rate of H_2 evolution on pure TiO_2 is extremely low. However, when the photogenerated electrons transfer from TiO_2 to the CoS particles, protons can be efficiently reduced to produce H_2 because CoS is a good cocatalyst for the reduction of protons. Moreover, intimate junctions can be formed between CoS and TiO_2 , which can facilitate the electron transfer from TiO_2 to CoS and reduce the electron and hole recombination.

4. Conclusion

Metal sulfide-modified TiO_2 catalysts were synthesized using the hydrothermal method. We found that H_2 formation on CoS/TiO_2 is considerably more efficient than on ZnS/TiO_2 and $\text{Bi}_2\text{S}_3/\text{TiO}_2$. The results showed that CoS/TiO_2 had the best photocatalytic activity in the H_2 and HCHO production reactions under 300 W Xe lamp irradiation. The enhanced activity can be attributed to the intimate junctions that are formed between CoS and TiO_2 , which can facilitate the electron transfer from TiO_2 to CoS and reduce the electron-hole recombination. The experimental results showed that a suitable amount of CoS could significantly enhance the photocatalytic activity of TiO_2 for H_2 and methanol production. This result is consistent with SEM analysis of the samples, which showed the highly dispersed nature of the 20 wt% CoS/TiO_2 sample. The maximum photocatalytic activity was obtained for 20 wt% CoS/TiO_2 , with hydrogen formation rate of 5.6 mmol/g/h and HCHO formation rate of 1.9 mmol/g/h with selectivity of 98.7%. Moreover, the CoS/TiO_2 photocatalyst showed good reusability and stability.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] M. Ni, M. K. H. Leung, D. Y. C. Leung, and K. Sumathy, "A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production," *Renewable and Sustainable Energy Reviews*, vol. 11, no. 3, pp. 401–425, 2007.
- [2] A. Kudo and Y. Miseki, "Heterogeneous photocatalyst materials for water splitting," *Chemical Society Reviews*, vol. 38, no. 1, pp. 253–278, 2009.
- [3] Z. Zou, J. Ye, K. Sayama, and H. Arakawa, "Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst," *Nature*, vol. 414, no. 6864, pp. 625–627, 2001.
- [4] C. Xu, W. Yang, Q. Guo, D. Dai, M. Chen, and X. Yang, "Molecular hydrogen formation from photocatalysis of methanol on anatase- TiO_2 (101)," *Journal of the American Chemical Society*, vol. 136, no. 2, pp. 602–605, 2014.
- [5] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.
- [6] K. Hashimoto, H. Irie, and A. Fujishima, " TiO_2 photocatalysis: a historical overview and future prospects," *Japanese Journal of Applied Physics*, vol. 44, no. 12, pp. 8269–8285, 2005.
- [7] J. Zhang, Q. Xu, Z. Feng, M. Li, and C. Li, "Importance of the relationship between surface phases and photocatalytic activity of TiO_2 ," *Angewandte Chemie International Edition*, vol. 47, no. 9, pp. 1766–1769, 2008.
- [8] J. Yu, W. Wang, B. Cheng, and B.-L. Su, "Enhancement of photocatalytic activity of mesoporous TiO_2 powders by hydrothermal surface fluorination treatment," *Journal of Physical Chemistry C*, vol. 113, no. 16, pp. 6743–6750, 2009.
- [9] S. G. Kumar and L. G. Devi, "Review on modified TiO_2 photocatalysis under UV/visible light: selected results and related mechanisms on interfacial charge carrier transfer dynamics," *The Journal of Physical Chemistry A*, vol. 115, no. 46, pp. 13211–13241, 2011.
- [10] R. Daghrir, P. Drogui, and D. Robert, "Modified TiO_2 for environmental photocatalytic applications: a review," *Industrial & Engineering Chemistry Research*, vol. 52, no. 10, pp. 3581–3599, 2013.
- [11] H. R. Liang and L. J. Guo, "Photocatalytic H_2 evolution under visible-light irradiation on modified TiO_2 catalysts," *Advanced Materials Research*, vol. 512–515, pp. 1426–1431, 2012.

- [12] X. Ren, X. Qi, Y. Shen et al., "2D co-catalytic MoS₂ nano-sheets embedded with 1D TiO₂ nanoparticles for enhancing photocatalytic activity," *Journal of Physics D: Applied Physics*, vol. 49, no. 31, article 315304, 2016.
- [13] P. Ganesan, A. Sivanantham, and S. Shanmugam, "CoS₂-TiO₂ hybrid nanostructures: efficient and durable bifunctional electrocatalysts for alkaline electrolyte membrane water electrolyzers," *Journal of Materials Chemistry A*, vol. 6, no. 3, pp. 1075–1085, 2018.
- [14] L. Cheng, Q. Xiang, Y. Liao, and H. Zhang, "CdS-based photocatalysts," *Energy & Environmental Science*, vol. 11, no. 6, pp. 1362–1391, 2018.
- [15] Z. Hu, H. Quan, Z. Chen, Y. Shao, and D. Li, "New insight into an efficient visible light-driven photocatalytic organic transformation over CdS/TiO₂ photocatalysts," *Photochemical & Photobiological Sciences*, vol. 17, no. 1, pp. 51–59, 2018.
- [16] N. L. Reddy, V. N. Rao, M. M. Kumari, P. Ravi, M. Sathish, and M. V. Shankar, "Effective shuttling of photoexcitons on CdS/NiO core/shell photocatalysts for enhanced photocatalytic hydrogen production," *Materials Research Bulletin*, vol. 101, pp. 223–231, 2018.
- [17] H. Yan, J. Yang, G. Ma et al., "Visible-light-driven hydrogen production with extremely high quantum efficiency on Pt-PdS/CdS photocatalyst," *Journal of Catalysis*, vol. 266, no. 2, pp. 165–168, 2009.
- [18] Q. Xiang, J. Yu, and M. Jaroniec, "Synergetic effect of MoS₂ and graphene as cocatalysts for enhanced photocatalytic H₂ production activity of TiO₂ nanoparticles," *Journal of the American Chemical Society*, vol. 134, no. 15, pp. 6575–6578, 2012.
- [19] Q. Wang, N. An, Y. Bai et al., "High photocatalytic hydrogen production from methanol aqueous solution using the photocatalysts CuS/TiO₂," *International Journal of Hydrogen Energy*, vol. 38, no. 25, pp. 10739–10745, 2013.
- [20] Y. Niu, P. Huang, F. Li et al., "Noble metal decoration and presulfation on TiO₂: increased photocatalytic activity and efficient esterification of *n*-butanol with citric acid," *International Journal of Photoenergy*, vol. 2016, Article ID 4618924, 12 pages, 2016.
- [21] S. Xie, Z. Shen, J. Deng et al., "Visible light-driven C–H activation and C–C coupling of methanol into ethylene glycol," *Nature Communications*, vol. 9, no. 1, article 1181, 2018.
- [22] Y. Sui, Q. Liu, T. Jiang, and Y. Guo, "Synthesis of nano-TiO₂ photocatalysts with tunable Fe doping concentration from Ti-bearing tailings," *Applied Surface Science*, vol. 428, pp. 1149–1158, 2018.
- [23] X. Fang, J. Song, T. Pu et al., "Graphitic carbon nitride-stabilized CdS@CoS nanorods: an efficient visible-light-driven photocatalyst for hydrogen evolution with enhanced photo-corrosion resistance," *International Journal of Hydrogen Energy*, vol. 42, no. 47, pp. 28183–28192, 2017.
- [24] Y. Zhang, N. Zhang, R. Tang Z., and Y.-J. Xu, "Graphene transforms wide band gap ZnS to a visible light photocatalyst. The new role of graphene as a macromolecular photosensitizer," *ACS Nano*, vol. 6, no. 11, pp. 9777–9789, 2012.
- [25] J. Cao, B. Xu, H. Lin, B. Luo, and S. Chen, "Novel heterostructured Bi₂S₃/BiOI photocatalyst: facile preparation, characterization and visible light photocatalytic performance," *Dalton Transactions*, vol. 41, no. 37, pp. 11482–11490, 2012.
- [26] X. Gao, G. Huang, H. Gao et al., "Facile fabrication of Bi₂S₃/SnS₂ heterojunction photocatalysts with efficient photocatalytic activity under visible light," *Journal of Alloys and Compounds*, vol. 674, pp. 98–108, 2016.
- [27] S. Yu, "Ultrasonic aerosol spray-assisted preparation of TiO₂/In₂O₃ composite for visible-light-driven photocatalysis," *Journal of Catalysis*, vol. 310, pp. 84–90, 2014.