1. Introduction

Energy and environmental issues are important topics on a global level. To tackle the issue of the depletion of fossil fuels and their environmental misdeeds, the exploration of renewable and clean energy resources and the development of eco-friendly practical systems for environmental remediation have been drawing increasing attention (Figure 1). Semiconductor photocatalyst systems can be used to split water into H₂ and O₂, to photo-reduce CO₂ into renewable fuels such as CH₃OH, CH₄, and CO, and to decompose various organic contaminations to remedy the environment. These methods use solar energy as the source of photons to promote reactions.¹ ² Photocatalytic reaction processes primarily involve three main steps: (1) the photogeneration of electron–hole pairs through the absorption of solar light of the energy larger than the band gap of photocatalyst, (2) the charge separation and migration onto the surface without recombination, and (3) the reduction/oxidation reaction on the surface of photocatalyst.¹ ³ ⁵ The efficiency of a photocatalyst is primarily determined by the balance of the thermodynamics and kinetics of these processes. It is difficult for a single-component photocatalyst to simultaneously possess wide light-absorption range and strong redox ability, because wide light-absorption range that needs to narrow the semiconductor bandgap is incompatible with strong redox ability that should widen the semiconductor bandgap. This is reason that a more negative potential of the conduction band (CB) and a more positive potential of the valence band (VB) are beneficial for the reduction and oxidation of reactants, respectively. Although some metal oxides (e.g., TiO₂ and WO₃) and non-oxides (e.g., CdS and Ta₃N₅) are widely used as photocatalysts, their performance of the photocatalytic reaction is still very low.¹ ² ⁶ The construction of heterostructured photocatalyst systems (usually type-II heterojunctions) that comprise multiple components or multiple phase is one effective strategy to improve photocatalytic efficiency because of the tunable band structures and efficient electron-hole separation and transportation.¹ ³ However, the redox ability of photoexcited electrons and holes on reaction sites are weakened, leading to lower redox ability.¹ ⁷ ⁸ Therefore, it is necessary to develop a novel photocatalytic system to overcome the aforementioned problems and significantly improve the efficiency of the photocatalytic reaction.

In nature, H₂O and CO₂ are converted into O₂ and carbohydrate through natural photosynthesis (NPS) in green plants, as shown in Figure 2. This photosystem, which looks like English letter “Z”, known as the Z-scheme, involves a two-step...
photoexcitation.\(^{[8–10]}\) Photosystem I (PS I) and photosystem II (PS II) harvest solar energy and pump electrons to a higher electronic state (excitation), which are connected in series with an electron transfer chain (electron mediator). The electrons in PS II flowed from the electron transport chain leads to the reduction of co-enzyme NADP\(^+\) into NADP that is used to fix CO\(_2\) into carbohydrate in the dark reaction, and the water oxidation occurs at a manganese calcium oxide cluster in PS II.\(^{[8–11]}\) The efficiency of charge separation in the reaction center of PS I protein is close to 100%. The artificial Z-Scheme system that mimics natural photosynthesis of green plant consists of two connected semiconductor photocatalysts, which has the merit of keeping electrons/holes with stronger reduction/oxidation abilities on different active sites. In a typical Z-scheme photocatalytic system, two different photocatalysts are combined using an appropriate shuttle electron mediator, as shown in Figure 3.\(^{[18]}\) Visible light can be utilized more efficiently because the range of solar energy for driving each photocatalyst is reduced, and electrons/holes with stronger reduction/oxidation abilities in PS I and PS II could be produced.\(^{[12,13]}\)

Figure 1. Schematic illustration of research field of photocatalysts.

Z-scheme water splitting was first reported by Bard et al. in 1979.\(^{[14]}\) Since then, Z-scheme water splitting has attracted considerable attention. Reversible redox mediators (e.g., Fe\(^{3+}\)/Fe\(^{2+}\), IO\(_3^-\)/I\(^-\), NO\(_3^-\)/NO\(_2^-\)) are usually served as electron transport chain in Z-scheme water splitting.\(^{[4]}\) However, backward reactions easily happen in the reversible redox mediator Z-scheme photocatalytic system, which are thermodynamically downhill in most cases. Redox mediators could cause undesirable backward reactions involving redox mediators, such as competitive oxidation of I\(^-\) by holes in the O\(_2\) evolution photocatalyst when using IO\(_3^-\)/I\(^-\) as redox mediator. Therefore, the reaction efficiency of reversible redox mediator Z-scheme photocatalytic system could be destroyed. In addition, the redox mediators also strongly absorb the visible light, reducing the light absorption of semiconductor photocatalysts. Thus, the Z-scheme photocatalytic systems without reversible redox pair mediators or with solid state electron mediators are necessary to be developed for water splitting.\(^{[13,14]}\) The noble-metal particles (such as Au, Ag) and graphene were explored

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as an solid electron mediator for the Z-scheme photocatalytic system. Thus, the aforementioned backward reactions can be perfectly avoided. Nevertheless, the noble-metal particles (such as Au, Ag) still strongly absorb part of the visible light due to surface plasmon resonance (SPR) effects, also reducing light absorption of semiconductor photocatalysts. So direct Z-scheme systems without the reversible redox pair mediators were also exploited in recent years.[27,33] Several reviews related to Z-scheme water splitting have been reported,[4,8,12] and all-solid-state Z-scheme photocatalytic systems without redox pair were especially summarized, which mainly exhibit the obvious differences of all-solid-state Z-scheme systems in the preparation methodology, working mechanism, properties and application.[7] Some Z-scheme examples were also partly presented in our previous reviews about heterostructured photocatalysts[3] and CO₂ photoreduction.[15]

Based on the discussion above, we know that the connection between two photocatalysts is crucial for constructing efficient Z-scheme photocatalytic systems. Many works studied different connection modes of Z-scheme photocatalytic systems.[13,17–20,22–41,43–97] The present review concisely summarizes and highlights recent state-of-the-art accomplishments of Z-scheme systems, which was categorized through diverse modes, including i) with shuttle redox mediators, ii) without electron mediators, and iii) with solid-state electron mediators. The challenges and prospects for future development of Z-scheme photocatalytic systems are also presented.

2. Z-Scheme Systems with Shuttle Redox Mediators

As shown in Figure 3, this kind of Z-scheme photocatalytic system consists of two different photocatalysts and an acceptor/donor (A/D) pair (so-called shuttle redox mediator).[4,8,16–18] No physical contact exists between PS I and PS II. Under solar light radicalization, the forward reactions on a H₂ evolution (PS I) photocatalyst occur as follows:

\[
2H^+ + 2e^- \rightarrow H_2 \text{ (photoreduction of H}^+ \text{to H}_2) 
\]

\[
D + nh^+ \rightarrow A \text{ (photooxidation of D to A)}
\]

The forward reactions on an O₂ evolution (PS II) photocatalyst should occur as follows:

\[
A + ne^- \rightarrow D \text{(CB of PS II)}
\]

\[
2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \text{ (VB of PS II)}
\]

However, the demonstration of the simultaneous evolution of H₂ and O₂ is extremely difficult in a Z-scheme system because the backward reactions also easily proceed over each photocatalyst,[7,17] as follows:

\[
A + ne^- \rightarrow D \text{(CB of PS I)}
\]

\[
D + nh^+ \rightarrow A \text{(VB of PS II)}
\]

The electron acceptor (A) and donor (D) react with the photogenerated electrons in the CB of PS I and holes in the VB of PS II, respectively, resulting in the obviously decrease in the effective number of photogenerated electrons and holes. Thus, it is critical to suppress the backward reactions involving redox mediators that are thermodynamically more favorable than water splitting. In 2010, Domen et al. succeeded in water splitting using a Z-scheme system consisting of Pt-loaded ZrO₂-TaON and Pt-loaded WO₃ as the H₂- and O₂-evolution photocatalysts, respectively, in the presence of an IO₃⁻/I⁻ redox mediator.[19] The undesirable backward reactions, such as oxidation of I⁻ ions on the Pt-loaded WO₃ and the reduction of IO₃⁻ on the Pt-loaded ZrO₂-TaON, were significantly minimized. As a result, the highest apparent quantum efficiency (AQE) of 6.3% at 420 nm was achieved. This high selectivity for the forward reactions in the Z-scheme system was also demonstrated by using Pt-SrTiO₃:Cr/Ta, Pt-WO₃, and the IO₃⁻/I⁻ redox mediator.[17] Additionally, the forward reactions in the Z-scheme

![Figure 2. Charge separation mechanism in natural photosynthesis.](image)

![Figure 3. Forward and backward reactions in a Z-scheme system with shuttle redox mediators.](image)
system were promoted by the presence of a nanoparticulate cocatalyst (e.g., Pt, Rh, NiO, RuO2), that was loaded onto the photocatalyst surface to produce active sites and reduce the activation energy for the surface chemical reactions.[6,13] The behavior of different cocatalysts (e.g., Pt, Rh, Ni, Ru, Fe2O3, and RuO2) loaded on SrTiO3:Rh/WO3 visible-light-driven Z-scheme photocatalysis systems for H2 and O2 evolution with Fe3+/Fe2+ as the electron mediator were investigated, and the water splitting was obviously enhanced in comparison with the non-loaded system.[20] The water splitting of the system using the Pt cocatalyst decreased as the partial pressures of the evolved H2 and O2 were increased. However, such deactivation was not observed for the system using the Ru cocatalyst due to the significant suppression of the backward reactions. Moreover, the selective catalysis is achieved via the introduction of a proper cocatalyst on the photocatalyst surface. Mn3O4, RuO2, IrO2, and CoO2 nanoparticles were found to function as O2 evolution cocatalysts.[21] For instance, RuO2-loaded TaON is an effective photocatalyst for O2 evolution to achieve water splitting in combination with Pt-loaded TaON as a H2 evolution photocatalyst with an IO3−/I− redox mediator.[22] TaON alone was not applicable for the O2 evolution due to the insufficiently competitive oxidation of I−. However, loading RuO2 on the TaON surface enables water oxidation even in the presence of I−.[4,22,23] IrO2-loaded Ta3N5 or Pt-BaTaO2N is another interesting example that allows water oxidation in the presence of IO3−/I−, respectively.[24,25] The choice of the reaction pH plays a key role in effectively improving the efficiency of the Z-scheme system.[4,17,18] A pH-dependent Z-scheme system based on Pt/ananite TiO2 and rutile TiO2 as a H2 evolution photocatalyst, respectively, achieved much higher evolution rates of H2 and O2 at pH > 9.[17]

All primary semiconductor-based Z-scheme systems with shuttle redox mediators are summarized in Table 1. Nevertheless, these Z-scheme systems have various negative effects, such as back reactions for the water splitting reaction. The redox mediators may also strongly absorb visible light, reducing the light absorption of the semiconductor photocatalysts. Additionally, it is often difficult to maintain long-term stability and active state for the redox mediators, resulting in a decrease in reaction rates. To avoid these disadvantages, Z-scheme systems without redox mediators have attracted much attention because they eliminate these limitations.[7,26]

3. Z-Scheme Systems Without Redox Mediators

A direct Z-scheme system without redox mediators was schematically illustrated in Figure 4a. Under solar light irradiation, the photoexcited electrons in PS II with a relatively low CB may recombine with the holes in PS I that have a relatively high VB at the solid heterostructure interface. Then, more oxidative holes and reductive electrons can be retained on different counterparts, resulting in an enhancement in the photocatalytic efficiency. Notably, the backward reactions in a Z-scheme system with redox mediators are primarily suppressed because of the absence of redox mediators. Furthermore, the shielding effect of the irradiated incident light that is caused by the redox mediators can also be significantly eliminated.

It is necessary to investigate the occurrence of the direct Z-scheme system instead of the type-II heterojunction mechanism (as shown in Figure 4b) when two semiconductors contact without redox mediators.[27] The type-II heterojunction facilitated the transfer of electrons from CB of semiconductor 1 (S 1) to that of semiconductor 2 (S 2) and the opposite transfer route of the holes. The different electron-hole transfer mechanisms between direct Z-scheme photocatalytic system and type-II heterojunction system could be investigated by photoluminescence (PL) spectra and transient time-resolved PL decay measurements. For instance, our group constructed ultrathin multilayer hollow spheres that consist of alternating TiO2, RuO2, and SrTiO3:Rh/WO3 visible-light-driven Z-scheme photocatalysis systems.

A pH-dependent Z-scheme system without redox mediators have attracted much attention because they eliminate these limitations.
Table 1. Z-Scheme photocatalyst system with shuttle redox mediators.

| PS I (available wavelength [nm]) | PS II (available wavelength [nm]) | Light source | Redox mediators | Application | Activity [μmol h⁻¹] | Efficiency(%) | Ref. (year) |
|---------------------------------|----------------------------------|--------------|-----------------|-------------|---------------------|---------------|------------|
| Fe²⁺ (<280)                     | RuO₂/WO₃ (<460)                  | Hg lamp (400 W) | Fe²⁺/Fe³⁺       | water splitting | H₂:38, O₂:15    |              | [16] (1997)|
| Pt/SrTiO₃:Cr-Ta (<700)          | Pt/WO₃ (<460)                   | Xe lamp (300 W) | I⁻/I₂⁻         | water splitting | H₂:0.21, O₂:0.11 | AQE = 0.1% (420 nm) | [64] (2001) |
| Pt/TiO₂-anatase (<400)          | TiO₂-rutile (<400)              | Hg lamp (400 W) | I⁻/I₂⁻         | water splitting | H₂:180, O₂:90   |              | [65] (2001) |
| Pt/SrTiO₃ (<520)                | BiVO₄ (<520)                    | Xe lamp (300 W) | Fe²⁺/Fe³⁺       | water splitting | H₂:15, O₂:7.2   | AQE = 0.3% (440 nm) | [66] (2004) |
| Pt/TaON (<500)                  | Pt/WO₃ (<460)                   | Xe lamp (300 W) | I⁻/I₂⁻         | water splitting | H₂:24, O₂:12    | AQE = 0.4 % (420 nm) | [67] (2005) |
| m-ZrO₂/TaON (<500)             | Pt/WO₃ (<460)                   | Xe lamp (300 W) | I⁻/I₂⁻         | water splitting | H₂:4.1, O₂:2    |              | [68] (2008) |
| Pt/SrTaO₃:Rh (<520)             | BiVO₄ (<520)                    | Xe lamp (300 W) | Fe²⁺/Fe³⁺       | water splitting | H₂:18.9, O₂:8.9 | AQE = 0.3% (420 nm) | [20] (2008) |
| Pt/H₂N₂NbO₇ (<750)             | IrO₂-Pt/WO₃ (<460)             | Xe lamp (300 W) | I⁻⁺/I⁻         | water splitting | H₂:2.1, O₂:1.0  |              | [70] (2009) |
| Pt/SrTiO₃ (<520)                | BiVO₄ (<520)                    | Xe lamp (300 W) | Fe²⁺/Fe³⁺       | water splitting | H₂:40, O₂:19    | AQE = 1.7% (420 nm) | [31] (2009) |
| Pt/ZrO₂/TaON (<520)            | Pt/WO₃ (<460)                   | Xe lamp (300 W) | I⁻/I₂⁻         | water splitting | H₂:7.5, O₂:3.8  | AQE = 6.3% (420 nm) | [19] (2010) |
| Pt/ZrO₂/TaON (<520)            | Ir/R-TiO₂/TaON (<600)          | Xe lamp (300 W) | I⁻/I₂⁻         | water splitting | H₂:7.0, O₂:1.0  |              | [24] (2010) |
| Pt/ZrO₂/TaON (<520)            | RuO₂/TaON (<520)               | Xe lamp (300 W) | I⁻/I₂⁻         | water splitting | H₂:8.0, O₂:3.0  |              | [23] (2011) |
| Pt/SrTiO₃:Rh (<520)             | Ru/SrTiO₂:In/V (<520)          | Xe lamp (300 W) | I⁻/I₂⁻         | water splitting | AQE = 0.33% (360 nm) |              | [71] (2012) |
| Pt/SrTiO₃:Cr/Ta (<550)          | Cs¹⁺–PbO₂/WO₃ (<460)           | Xe lamp (300 W) | I⁻⁺/I⁻⁻⁻/I⁻⁻⁻⁻ | water splitting | H₂:40, O₂:20    | AQE = 1.5% (420 nm) | [72] (2013) |
| Ru/SrTiO₃:Rh (<520)             | BiVO₄ (<520)                    | Xe lamp (300 W) | [Co(bpy)₃]³⁺/²⁺ and [Co(phen)]³⁺/²⁺ | water splitting | H₂:94, O₂:38   | AQE = 2.1% (420 nm) | [73] (2013) |
| Ru/SrTiO₃:Rh (<520)             | BiVO₄ (<520)                    | Xe lamp (300 W) | Fe²⁺/Fe³⁺       | water splitting | H₂:1.2, O₂:0.6   | AQE = 4.2% (420 nm) | [74] (2013) |
| BaZrO₃–BaTaO₃:N (690)           | PrO₂/WO₃ (<460)                 | Xe lamp (300 W) | I⁻/I₂⁻         | water splitting | H₂:150, O₂:62    |              | [75] (2013) |
| Pt/Sm₂Ti₂S₂O₅ (<650)            | TiO₂-rutile (<387)             | Hg lamp (450 W) | I⁻/I₂⁻         | water splitting | H₂:45, O₂:16   |              | [76] (2014) |
| Pt/g-C₃N₄ (<450)                | Pt/WO₃ (<460)                   | Xe lamp (300 W) | I⁻/I₂⁻         | water splitting | H₂:74, O₂:37   |              | [77] (2014) |
| Pt/carbon nanodots              | WO₃ (<460)                     | Xe lamp (300 W) | I⁻/I₂⁻         | H₂-evolution    | H₂:1330 |              | [78] (2015) |
| Pt/MgTaO₃:N₆/TaON (<750)       | PrO₂/WO₃ (<460)                 | Xe lamp (300 W) | I⁻/I₂⁻         | water splitting | H₂:108.3, O₂:55.3 | AQE = 6.8% (420 nm) | [79] (2015) |

Notes:

- AQE = apparent quantum efficiency.

Suspension of CdCl₂ and Zn(OH)₂ precipitate, resulting in a Z-scheme ZnO/CdS photocatalytic system. ZnO/CdS are highly active photocatalysts for H₂ evolution under simulated solar light irradiation, due to the strong phase interaction by the binding energy shift of Zn 2p<sub>3/2</sub>, Cd 3d<sub>3/2</sub>, O 1s, and S 2p in the ZnO/CdS heterostructure in contrast to the pure ZnO and CdS. Z-scheme BiVO₄/g-C₃N₄ composites that the facet coupling occurred between the g-C₃N₄ (002) and BiVO₄ (121) were obtained by calcination of a mixture of appropriate amounts of BiVO₄ and g-C₃N₄ at 400°C for 4 h. Similarly, other Z-scheme composites, such as MoO₃/g-C₃N₄, ZnO/g-C₃N₄, and WO₃/g-C₃N₄, have also been synthesized.
through calcination process. Additionally, hydrothermal reactions were extensively applied to the formation of direct Z-scheme systems. Direct Z-scheme Si/TiO₂ composites were fabricated via a facile hydrothermal reaction with tetraethyl titanate and as-prepared Si nanospheres.

The direct Z-scheme system can work in both liquid-phase and gas-phase environments, which are widely used to split water, photoreduce CO₂, and decompose various organic contaminants (see Table 2). Solar-driven water splitting has been achieved under simulated sunlight using direct Z-scheme Si/TiO₂ nanotree-structures. The photogenerated electrons in Si and the holes in TiO₂ moved to the surface to perform water splitting as the photogenerated holes in Si and the electrons in TiO₂ recombined at the Ohmic contact between the Si and TiO₂. The solar-to-fuel conversion efficiency was approximately 0.12%, which is comparable to that of natural photosynthesis.

Additionally, the Z-scheme Si/TiO₂ consisted of porous Si nanospheres and TiO₂ nanosheets that achieved high activity towards CO₂ reduction into methanol with a maximum photoconversion efficiency of 18.1%. The direct Z-scheme NaNbO₃/WO₃ photocatalyst exhibited a relatively much higher photocatalytic activity, and the rate constants of RhB and MB degradation for NaNbO₃/WO₃ were 4.9 times and 3.4 times than that of pure WO₃, respectively. This attributed to the fast recombination between the photogenerated holes of NaNbO₃ and the photogenerated electrons of WO₃. As a promising photocatalyst, graphite-like carbon nitride (g-C₃N₄), which consists of only carbon and nitrogen, is a sustainable, cost-effective and environmental-friendly semiconductor that has attracted extensive interest. The combination of g-C₃N₄ with other appropriate semiconductors for construction of a direct Z-scheme system can effectively improve the photocatalytic performance. Recently, a direct Z-scheme g-C₃N₄/AgBr photocatalyst was prepared by loading AgBr nanoparticles on a protonated g-C₃N₄ matrix. Fast recombination may occur between the photogenerated electrons in the CB of AgBr and the photogenerated holes in the VB of g-C₃N₄. As a result, the photodegradation rate of methyl orange (MO) over the g-C₃N₄/AgBr photocatalyst was 33.8 and 2.1 times higher than that over pure g-C₃N₄ and AgBr samples, respectively.

Although direct Z-scheme systems effectively improve photocatalytic activities due to the recombination of photoexcited electrons from the CB of PS II and holes from the VB of PS I at the interface, the photoexcited carrier transport process at the interface between PS II and PS I is often poor due to surface relaxation and the recombination of charge carriers within each component. Therefore, the design of a new structural system with pathways for quick transport of charge carriers at the interface is highly desired.

4. Z-Scheme Systems with Solid State Electron Mediators

As shown in Figure 6, the Z-scheme photocatalytic system consists of two different photocatalysts (PS I and PS II) and a solid electron mediator at the interface of two semiconductors, and their photocatalytic applications were listed in Table 3. Noble-metal particles (such as Au, Ag) and reduced graphene oxide...
(RGO) were explored as electron mediators for the Z-scheme system, and a high efficiency of the charge-carrier separation and transport can be achieved at the interface of the two semiconductors. Under UV irradiation, the photoexcited electrons in the CB of TiO₂ transferred to Au and then to the VB of CdS, subsequently recombined with the holes photogenerated in CdS. Simultaneously, the photogenerated holes in the VB of CdS were transferred to the VB of SiC, resulting in a high efficiency of the electron-hole separation and an enhancement in the photocatalytic activities. The solid-state Z-scheme system of ZnRh₂O₄/Ag/Ag₁–ₓSbO₃–y was developed to split pure water under visible light irradiation. In this system, Ag acted as a solid-state electron mediator for the transfer of electrons from the conduction band of Ag₁–ₓSbO₃–y to the valence band of ZnRh₂O₄. As a result, the water-splitting activity of ZnRh₂O₄/Ag/Ag₁–ₓSbO₃–y was higher than that of ZnRh₂O₄/Ag₁–ₓSbO₃–y. With Ag nanoparticles as the solid state electron mediator, other Z-scheme systems, such as AgₓCO₃/Ag/AgBr, AgₓPO₄/Ag/SiC, and α/β Bi₂O₃/Ag/AgCl, have also been reported enhancement in their photocatalytic activities.

Notably, noble-metal nanoparticles (Au, Ag) used as photosensitizers can strongly absorb visible light due to their high absorption coefficients in the visible-light region. The addition of noble-metal nanoparticles to semiconductor photocatalysts can enhance the light harvesting and charge separation, leading to improved photocatalytic activities. For example, the introduction of Ag nanoparticles into TiO₂ can significantly increase the photocatalytic activity for the degradation of RhB under UV light irradiation. The high photocatalytic activity is attributed to the strong light absorption and charge separation of the Ag nanoparticles, which can enhance the photocatalytic performance of the composite materials.

In summary, the combination of noble-metal nanoparticles with semiconductors can synergistically improve the photocatalytic performance under visible-light irradiation. The design of Z-scheme systems with noble-metal nanoparticles has opened up new possibilities for the development of advanced photocatalysts.

### Table 2. Direct Z-Scheme systems.

| PS I (available wavelength [nm]) | PS II (available wavelength [nm]) | Light source | Application | Activity | Efficiencya) | Ref. (year) |
|---------------------------------|---------------------------------|--------------|-------------|----------|---------------|------------|
| CaFe₂O₄ (≤700) |WO₃ (≤460) |Xe lamp (150 W)| photodegradation | CH₃CHO degradation | [30] (2013) |
| NaNbO₃ |WO₃ (≤460) |Hg lamp (375 W)| photodegradation | RhB degradation | DE = 96% (80 min) | [32] (2013) |
| g-C₃N₄ (≤450) |TiO₂ (≤387) |UV lamp (15 W)| photodegradation | HCHO degradation | DE = 94% (1 h) | [80] (2013) |
| Si (≤1107) |TiO₂ (≤387) |Xe lamp (300 W)| photodegradation | RhB degradation | DE = 99% (1 h) | [39] (2014) |
| g-C₃N₄ (≤450) |ZnO·N (395) |Xe lamp (300 W)| photodegradation | RhB degradation | DE = 99% (1 h) | [37] (2014) |
| g-C₃N₄ (≤450) |SiTiO₃·N (≤420) |Xe lamp (300 W)| photodegradation | RhB degradation | DE = 98% (1 h) | [44] (2014) |
| g-C₃N₄ (≤450) |MoO₃ (≤450) |Xe lamp (350 W)| photodegradation | MO degradation | DE = 91% (2 h) | [36] (2014) |
| g-C₃N₄ (≤450) |BiVO₄ (≤375) |Xe lamp (300 W)| photodegradation | RhB degradation | DE = 99% (1 h) | [81] (2014) |
| AgI (≤521) |β-Bi₂O₃ (≤443) |UV-LED (3W)| photodegradation | MO degradation | DE = 99% (1 h) | [82] (2015) |
| Bi₂TiO₅ (≤550) |g-C₃N₄ (≤450) |Xe lamp (300W)| photodegradation | RhB degradation | DE = 99% (20 min) | [83] (2015) |
| g-C₃N₄ (≤450) |BiVO₄ (≤520) |Xe lamp (500W)| photodegradation | RhB degradation | DE = 85% (5 h) | [33] (2015) |
| g-C₃N₄ (≤450) |AgBr (≤490) |Xe lamp (300W)| photodegradation | MO degradation | DE = 78.9% (2 h) | [43] (2015) |
| CuO (≤730) |TiO₂ (≤387) |Hg lamp (250W)| CO₂ Reduction | CH₄:0.1 μmol g⁻¹h⁻¹ | [27] (2015) |
| GdS (≤540) |TiO₂ (≤387) |Hg lamp (250W)| CO₂ Reduction | C₆H₁₀O: 20 μmol g⁻¹h⁻¹ | [34] (2014) |
| Si (≤1107) |TiO₂ (≤387) |Xe lamp (300W)| CO₂ Reduction | CH₃OH | PE = 18.1% | [39] (2014) |
| Si (≤1107) |TiO₂ (≤387) |Xe lamp (300W)| CO₂ Reduction | CH₃OH:0.14 μmol g⁻¹h⁻¹ | [39] (2014) |
| Bi₂WO₆ (≤470) |g-C₃N₄ (≤450) |Xe lamp (300W)| CO₂ Reduction | CO:5.19 μmol g⁻¹h⁻¹ | [40] (2015) |
| GdS (≤500) |TiO₂·O₂ (≤326) |Xe lamp (300W)| CO₂ Reduction | CH₄:0.1 μmol g⁻¹h⁻¹ | [27] (2015) |
| GdS (≤540) |ZnO (≤382) |Xe lamp (300W)| water splitting | H₂:3870 μmol g⁻¹h⁻¹ | [33] (2009) |
| Si (≤1060) |TiO₂ (≤387) |Xe lamp (300W)| water splitting | H₂:875 μmol g⁻¹h⁻¹ | CE = 0.12% | [41] (2013) |
| Ru/SrTiO₃:Rh (≤520) |Ir/Co₃O₄Ta₃N₃ (≤600) |Xe lamp (300W)| water splitting | H₂:23 μmol g⁻¹h⁻¹ | [85] (2013) |
| g-C₃N₄ (≤450) |WO₃ (≤460) |Xe lamp (300W)| water splitting | H₂:110 μmol g⁻¹h⁻¹ | AQE = 90.0% (405 nm) | [38] (2014) |

a) PE = photon efficiency; CE = conversion efficiency; AQE = apparent quantum efficiency.
The photogenerated electrons of H$_2$WO$_4$ transferred to the Ag nanoparticles because of the SPR effects. Meanwhile, photoinduced electrons and holes. Simultaneously, the holes of H$_2$WO$_4$ oxidized organic substances. However, the plasmon-induced electrons of the Ag nanoparticles were injected into the CB of AgCl to reduce oxygen. Other visible-light-driven plasmonic Z-scheme systems, including Ag/AgCl/ Bi$_2$O$_3$/TiO$_2$, Ag/AgCl/ZnO, and Ag/AgCl/BiOCl, have also been investigated. In these visible-light-driven plasmonic Z-scheme systems, PS II or PS I is photoexcited, and the SPR effect of the Ag nanoparticles became significant for the Z-scheme photocatalytic activities. However, when both PS II and PS I are photoexcited, Ag nanoparticles primarily act as the electron mediator.

In addition to the noble metals discussed above, some low-cost nonmetal materials and metal oxides with excellent conductivities can also be used as electron mediators in solid state Z-scheme systems. RGO was employed as a solid-state electron mediator to promote electron transfer between the photocatalyst particles in the Z-scheme system. Kudo et al. reported a solid state Z-scheme system (BiVO$_4$/RGO/ (Ru/SrTiO$_3$)/Rh) for water splitting. Under visible light irradiation, the RGO provides pathways for the photogenerated electrons in BiVO$_4$ and the holes in Ru/SrTiO$_3$/Rh to recombine, leaving holes in BiVO$_4$ and electrons in Ru/SrTiO$_3$/Rh to split the water. This “Z” mechanism of electron flow enhanced the charge separation efficiency, resulting in enhancement of the photocatalytic activities. Recently, Kudo et al. also demonstrated that RGO was used to construct Z-scheme systems that consist of various metal sulphides. The Z-scheme system composed of CuGaS$_2$ and RGO-TiO$_2$ continuously splits water into H$_2$ and O$_2$ for 12 h, producing a 1.3% apparent quantum yield under 380 nm of monochromatic light irradiation. Our group fabricated a Fe$_5$V$_3$O$_{11}$/RGO/CdS Z-scheme system that perpendicularly grew on a stainless-steel mesh for the photocatalytic reduction of CO$_2$ into methane. The advantage over the precedent powder Z-scheme systems is the presence of an “artificial lawn” that may provide a suggestive model for designing an integrated system for practical applications. Additionally, indium–tin oxide (ITO), W, and Cd may also be suitable for the construction of CaFe$_2$O$_4$/ITO/WO$_3$, WO$_3$/W/PbBi$_2$NbxTi$_{y}$O$_9$, and ZnO/Cd/CdS Z-scheme systems, respectively. The enhanced photocatalytic activity of these systems is attributed to the fast recombination of photogenerated holes in PS I and electrons in PS II within the conductive support.

5. Summary and Perspectives

Photocatalysis is a promising avenue for solving environmental and energy issues in the future, which is attracting an ever-growing number of scientists to this field. Thus far, the development of photocatalysts with high efficiency, long-term stability, and at a low cost is the main challenge for their practical application, and it is difficult for a single-component photocatalyst to simultaneously possess all of these features. The formation of Z-scheme photocatalytic systems effectively expands the utilization of visible light, improves the separation/transportation of the charge carriers, and substantially enhances the efficiency of the photocatalytic activities.

Z-scheme systems with shuttle redox mediators are primarily used for efficient water splitting. In this system, the effective separation of charge carriers occurs via recyclable redox reactions of the shuttle redox mediators. However, Z-scheme systems with shuttle redox mediators have various negative effects, such as back reactions, visible light absorption of the redox mediators, and short-term stability. Z-scheme systems with solid-state electron mediators typically suppress the above shortcomings because of the absence of redox mediators. Solid-state electron mediators provide a pathway for the photogenerated electrons in PS II and the holes in PS I to quickly travel and recombine, leaving more electrons in PS I and more holes in PS II to participate in the redox reaction. Additionally, the SPR effect of metal nanoparticles (Au, Ag) also plays an important role in Z-scheme systems. When PS II or PS I is photoexcited, the SPR effect of metal nanoparticles becomes significant for Z-scheme photocatalytic activities. However, when both PS II and PS I are photoexcited, the metal nanoparticles mainly act as electron mediators. The contact interface of PS I–PS II has a catalytic activity of these systems is attributed to the fast recombination of photogenerated holes in PS I and electrons in PS II within the conductive support. A high-quality interface of PS I–PS II facilitates the transfer of photogenerated charge carriers across the interface, resulting in enhancement of the photocatalytic performance. As the increasing amount of literatures presented direct Z-scheme system, it must be strict and careful for distinguishing the direct Z-scheme system.
The in situ technique was applied for the analysis of the difference in anisotropic photogenerated charge separation on different facets of a single BiVO₄ photocatalyst. Moreover, Li’s group applied spatially resolved surface spectroscopy (SRSSP) to obtain direct evidence of highly anisotropic photogenerated charge separation on different facets of a single BiVO₄ photocatalyst. From this technique, it was found that the photocatalyst exhibited excellent photodegradation efficiency for a variety of organic dyes and pollutants.

| PS I (available wavelength [nm]) | PS II (available wavelength [nm]) | Light source | Electron mediators | Application | Activity | Efficiency | Ref. YEAR |
|-------------------------------|-------------------------------|--------------|-------------------|-------------|----------|------------|-----------|
| AgBr (>490) | Bi₂WO₆ (<470) | Xe lamp (300 W) | Ag | photodegradation | Procion red degradation | DE = 85% (1 h) | [86] (2009) |
| CdS (<540) | TiO₂ (<387) | Hg lamp (20 W) | Au | photodegradation | MB degradation | DE = 72% (2 h) | [87] (2009) |
| CaFe₂O₄ (<670) | WO₃L₅ (<660) | Xe lamp (150 W) | Ag | photodegradation | CH₃CHO degradation | DE = 99% (48 h) | [63] (2009) |
| AgCl (<382) | H₂WO₄·H₂O (<500) | fluorescence lamp (55 W) | Ag | photodegradation | MO degradation | DE = 87% (4 h) | [54] (2011) |
| AgBr (<490) | BiOBr (<427) | Xe lamp (500 W) | Ag | photodegradation | RhB degradation | DE = 99% (44 min) | [57] (2012) |
| AgI (<521) | AgBr (<490) | Xe lamp (500 W) | Ag | photodegradation | MO degradation | DE = 97% (16 min) | [88] (2012) |
| AgCl (<382) | TaON (<453) | Xe lamp (300 W) | Ag | photodegradation | RhB degradation | DE = 96.6% (140 min) | [89] (2013) |
| AgI (<521) | Ag₃PO₄ (<321) | Xe lamp (500 W) | Au | photodegradation | RhB degradation | DE = 80% (1 h) | [91] (2015) |
| AgCl (<382) | Bi₂O₃ (<540) | Xe lamp (300 W) | Ag | photodegradation | RhB degradation | DE = 99% (30 min) | [52] (2015) |
| g-C₃N₄ (<450) | Ag₃PO₄ (<312) | Xe lamp (300 W) | Ag | photodegradation | MO degradation | DE = 97% (15 min) | [50] (2015) |
| SiC (<480) | Pt/TiO₂ (<387) | Xe lamp (300 W) | Cu | CO₂ reduction | HCOOH: 0.22 μmol cm⁻² h⁻¹ | AQE = 0.09% (365 nm) | [92] (2011) |
| InP/MCE₂₋₄ + MCE₄ (918) | Reduced SrTiO₃ (<400) | Solar simulator (AM1.5) | Ag | CO₂ reduction | HCOOH: 0.48 μmol h⁻¹ | CE = 0.14% | [93] (2013) |
| Pt/Fe₂V₂O₉ (111) (<677) | Cds (<540) | Xe lamp (300 W) | RGO | CO₂ reduction | CH₃OH: 1.57 μmol g⁻¹ h⁻¹ | [48] (2015) |
| g-C₃N₄ (<450) | Ag₃PO₄ (<312) | Xe lamp (300 W) | Ag | CO₂ reduction | C₂H₅OH:57.5 μmol g⁻¹ h⁻¹ | [94] (2015) |
| PbBi₂Nb₁₃Ti₁₀O₃₄ (430) | WO₃ (<460) | Xe lamp (450 W) | W | water splitting | H₂: 493.1 μmol g⁻¹ h⁻¹ | [62] (2006) |
| Pt/CdS (<540) | TiO₂ <400 | Xe lamp (500 W) | Au | water splitting | H₂: 10 μmol g⁻¹ h⁻¹ | [26] (2006) |
| Pt/CdS (<540) | TiO₂₋ₓCₓOₓ (477) | Xe lamp (300 W) | Au | water splitting | H₂: 433.2 μmol g⁻¹ h⁻¹ | [47] (2011) |
| Ru/SrTiO₃:Rh (<520) | BiVO₄ (<520) | Xe lamp (300 W) | RGO | water splitting | O₂: 5.5 μmol g⁻¹ h⁻¹ | [61] (2011) |
| Cds (<540) | ZnO (<387) | Xe lamp (300 W) | Cds | water splitting | H₂: 1920 μmol g⁻¹ h⁻¹ | [95] (2012) |
| Cds (<540) | TiO₂ (<387) | Xe lamp (750 W) | Au | water splitting | H₂: 64 μmol g⁻¹ h⁻¹ | [96] (2013) |
| ZnRh₂O₄ (<1033) | Ag₃SbO₄₋ₓ (<460) | Xe lamp (300 W) | Ag | water splitting | H₂: 0.0168 μmol g⁻¹ h⁻¹ | [51] (2014) |
| Ru/SrTiO₃:La/Rh (<500) | Ir/CoO₃/Ta₂O₅ (<600) | Xe lamp (300 W) | Ir | water splitting | O₂: 0.0084 μmol g⁻¹ h⁻¹ | AQE = 1.1% (420 nm) | [97] (2014) |
| CuGa₂ (<520) | TiO₂ (<387) | Xe lamp (300 W) | RGO | water splitting | H₂: 19.8 μmol g⁻¹ h⁻¹ | AQE = 1.3% (380 nm) | [59] (2015) |

*MB = methylene blue; MO = methyl orange; RhB = rhodamine B; AO7 = acid orange 7. **DE = degradation efficiency; CE = conversion efficiency; AQE = apparent quantum efficiency.
may also be applicable to detect the charge transfer process in direct Z-scheme system.\[28\]

Great progress has been achieved in the investigation of Z-scheme systems. However, the photocatalytic reaction is a complex process, and there are many important aspects that need further research, including developing new photocatalytic materials, fundamentally understanding the separation and transport of charge carriers on the interface, and understanding photocatalytic reaction pathways. Therefore, a greater knowledge of the Z-scheme photocatalytic mechanism and the exploration of new materials are indispensable for making substantial breakthroughs for the practical application of photocatalysts. In this regard, several key considerations could be concerned, including: i) a deep understanding of processes, such as the charge carrier transfer processes and the photocatalytic reaction pathways. The research would integrate experimental and computational approaches to evaluate photocatalytic activity, and would advance fundamental understanding of Z-scheme photocatalytic mechanism. The transient time-resolved luminescence decay measurements are well applied to analyze the behavior of photogenerated charge carriers, due to the high time resolution. Surface photovoltaic technique is another advanced technology for probing into the charge carrier transfer processes. ii) The shuttle redox mediators or solid-state electron mediators of Z-scheme system plays an important role in charge carrier transportation. It is urgent to develop new shuttle redox mediators or solid-state electron mediators for solving unfortunate problem, such as backward reactions and light absorption of mediators. iii) Exploitation of new Z-scheme photocatalytic system is also desired to avoid the mentioned problems in the inorganic Z-scheme photocatalytic system. A hybrid Z-scheme by integrating BiVO₄ and a platinized protein photosystem I (PSI) in an all-solid-state was constructed for H₂ evolution without redox mediators. This hybrid system provides a new means of using a photosynthetic protein as a practical material in the design of a photocatalytic system.\[29\]

Although the conversion efficiency is still low at the present stage, the Z-scheme photocatalytic system that mimics the natural photosynthesis in green plants may be the most promising photocatalytic system in photocatalytic field. It is sincerely expected that multiple collaboration for this rapidly evolving field can lead to a breakthrough in the efficiency for the commercialization and industrialization.

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