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Review

Advances in designing heterojunction photocatalytic materials

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ABSTRACT

Under the background of increasing energy crisis and global warming, semiconductor-based photocatalysis has received tremendous attention due to its potential application in green energy production, CO₂ reduction and pollutant degradation. The photocatalytic activity of semiconductors, however, remains low due to issues like fast recombination of photo-generated electron-hole pairs, limited electron mobility, restricted optical absorption or insufficient active sites. Designing appropriate heterojunctions is proved to be a promising method to address most of these issues and thus to improve the photocatalytic performance. In this review, the working mechanism of various heterojunctions is presented systematically. The most recent advances of strategies in designing and preparing efficient heterojunction photocatalysts are further summarized and some perspectives on the future directions in this field are provided.

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1. Introduction

Technology explosion has made the human society unprecedentedly convenient and civilized since the first industrial revolution. Along with the rapid development of the whole world, however, major threatens that can influence millions of people are buried. Examples are energy crisis, environment pollution and global warming. On May 11, 2019, Mauna Loa Observatory reported that the CO₂ level in the atmosphere had surpassed 415 ppm, which is the highest record through the whole human history. Tong et al. suggested the energy infrastructure has to be updated if the mean global warming is to be limited to 2 °C [1]. Successively, EU announced climate emergency in November 2019. Thus, it is urgent to develop green energy technologies to minimize the usage of fossil fuels and

reduce the production of pollutants [2,3]. Photocatalysis is one of the most promising candidates to address these issues, which can directly utilize solar energy to produce hydrogen from water splitting [4–8], to convert CO₂ into valuable chemicals [9–13] (such as CH₄, CO, CH₃OH, etc.), to degenerate organic pollutants [14–17], and to facilitate organic synthesis [18–23], as shown in Fig. 1.

Numerous semiconductors have been proposed as candidate photocatalysts and have been well studied, such as TiO₂ [24–29], CdS [30–35], ZnO [36–38], BiVO₄ [39–41], C₃N₄ [42–50] and so on. However, these semiconductors suffer from some drawbacks that hinder their practical application, which motivates the development of heterojunction-based photocatalysts. For example, TiO₂ and ZnO possess a band gap of ~3.2 eV, which corresponds to the ultraviolet radiation. Thus,

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Fig. 1. Versatile applications of photocatalysis.

TiO₂ or ZnO can only be excited by a small portion of solar energy. To boost the light utilization, one way is to introduce doping energy level in the band gap of the wide-bandgap semiconductors. Metal elements (such as Co, Ni, Cr etc.) or nonmetal elements (such as C, N, S etc.) have been used to dope ZnO or TiO₂, to improve their visible absorption [51–54]. On the contrary, CdS, Cu₂O, BiVO₄ and some others possess a band gap in the visible range inherently. A narrower band gap can prompt the absorption of solar energy. However, the narrower band gap reduces the reducing/oxidizing ability of the photogenerated electrons/holes inevitably. Another critical concern that limits the photocatalytic activity of these semiconductors is the fast recombination rate of photogenerated electron-hole pairs. For instance, the lifetime of excitons in ZnO is estimated to be several hundreds of picoseconds [55,56], which is too short for redox reactions to efficiently utilize the electron-hole pairs.

To suppress the recombination of electron-hole pairs and retain their reducing and oxidizing ability, special strategies are required to design optimal photocatalysts. Heterojunction design has become one of the most promising approaches, with benefits of high light harvesting, retarded electron-hole recombination and fast charge transportation. Various heterojunction materials have been prepared and proved to be effective within this framework. Generally, those heterojunctions can be categorized according to the adjacent band structures into several types: p-n heterojunction, conventional type II heterojunction, Schottky heterojunction and S-scheme heterojunction. Compared with others, the recent proposed S-scheme heterojunction is a young and competent strategy that inspires lots of works in the past years [57,58]. Beyond those aforementioned, there are two special heterojunctions, namely the surface heterojunction and graphene-based heterojunction. Different lattice planes of a crystal can exhibit very distinct band structures. Thus, a band alignment similar to that of a heterojunction can be formed within a single-crystalline semiconductor with different exposed facets, which could enhance largely the photocatalytic activity of the semiconductor. Graphene possesses unique band structure and the huge specific surface area, which makes it a promising material for the fabrication of efficient

photocatalysts. The band structure of graphene can be tuned through versatile ways, enabling the possibility of forming various types of heterojunctions with other semiconductors. In addition, the high electrical conductivity and large surface area make graphene a suitable material for the loading of photocatalysts, improving the overall activity. Composites based on graphene have also become a vital branch of the photocatalyst family.

In this review, we aim to present the most recent advances in the design and preparation of heterojunction photocatalysts, to summarize the basic strategies for achieving high-performance heterojunction photocatalysts and to give some perspectives on the future opportunities toward the development of highly efficient photocatalytic materials. We will first discuss the principles why heterojunctions can facilitate the photocatalytic efficiency. Then, the above-mentioned types of heterojunctions will be introduced respectively. In the end we will give a summarization and predict some future opportunities.

2. Mechanism and principle

Generally speaking, a photocatalyst-mediated redox reaction includes four processes, as illustrated in Fig. 2. (1) The photocatalyst absorbs solar energy under light illumination, with the excitation of electron-hole pairs. Thereafter, the solar energy is converted into energy stored in the excitons. (2) The photo-generated electrons and holes migrate to the surface of the photocatalyst. (3) The photocatalyst adsorb reactants on its surface. (4) The reactants are reduced/oxidized by electrons/holes and the products desorb from the photocatalyst surface. After this step, the photo-generated excitons are eliminated, and the stored energy is finally converted into chemical energy saved in the products. The photocatalyst returns to the initial state and is ready to another reaction cycle. Unfortunately, the second step encounters a serious competing process. Most generated electron-hole pairs tend to recombine to emit light or dissipate as heat, instead of migrating to the surface and participating in redox reactions. The recombination of electron-hole pairs is the main obstacle that hinders the improvement of the photocatalytic efficiency, and thus the prior issue heterojunctions are expected to address.

Fast separation of photo-generated electrons and holes is

Fig. 2. Schematic illustration of a photocatalytic redox reaction.

required to prevent their recombination. A rational way to achieve this is providing lower energy level to accommodate the excited electrons or holes. When two semiconductors with different Fermi levels contact closely, the electrons in the semiconductor with higher Fermi level will flow to the other semiconductor to reduce the total energy of the whole system. Consequently, net charges accumulate at the sides of the contacting interface, which makes the originally higher Fermi level lower and the originally lower Fermi level higher. The net electron flow stops until the electrochemical potential of the two semiconductors equals with each other. Meanwhile, the electronic band of the contacting semiconductor bends over in subject to the movement of Fermi levels, generating different forms of band alignments. Some typical band alignments are shown in Fig. 3 with the possibility and pathway of recombination. Among the conventional heterojunctions, the type II heterojunction is more favorable for the separation of electron-hole pairs. For type I heterojunction, the photo-generated electrons and holes can transfer to the relatively lower energy levels, respectively. However, they still accumulate in the same material, with a high possibility to recombine. For type III heterojunction, the energy bands of the two contacting semiconductors do not overlap, which is not suitable for the electron-hole separation and the charge transportation. For type II heterojunction, the electrons and holes can transfer to lower energy levels that exist in different materials. Thus, electron-hole pairs can be separated efficiently and participate in the successive redox reactions. Appropriate band overlap that enables electrons and holes to accumulate in different materials is essential for the design of efficient heterojunction photocatalysts.

From the viewpoint of reaction dynamics, the type II heterojunction is not perfect yet, since it accumulates electrons/holes at the relatively lower energy levels, which means reduced potential and thus weaker reducing/oxidizing ability of the electrons/holes. It would be preferred if the photogenerated electrons and holes can stay at the higher energy level and participate in following redox reactions. The S-scheme pathway provides a strategy to design heterojunctions with full redox potential. The band structure of a S-scheme heterojunction is

Fig. 3. Schematic illustration of the band structure of typical conventional heterojunctions and S-scheme heterojunction.

shown in Fig. 3. Compared with the type II heterojunction, the band structure of S-scheme heterojunction is similar. However, the recombination pathway in S-scheme heterojunction is different. A S-scheme heterojunction is composed by a reduction-type photocatalyst semiconductor and an oxidation-type photocatalyst semiconductor. To balance the Fermi level of the contacting semiconductors, an internal field is established which drives the photogenerated electrons to flow from the conduction band of the oxidation-type semiconductor to the valence band of the reduction-type semiconductor, consuming the corresponding photogenerated holes. As a result, electrons and holes locating at the lower energy levels are more likely to recombine, leaving the relatively useful electrons and holes with higher potential toward redox reactions. Hence, the S-scheme heterojunction can separate electron-hole pairs and retain full redox potential at the same time.

Besides electron-hole separation through providing lower energy levels, which is driven inherently by electrochemical potential, electrical fields can also behave as a driving force that facilitates the electron-hole separation. For example, an internal electrical field can be built in a PN heterojunction, as shown in Fig. 4. The holes in the p zone will diffuse to the n zone until the Fermi level equals with each other, leaving net negative charges in the p zone. Conversely, there are net positive charges accumulating in the n zone. Therefore, an internal field is formed pointing from the n zone to the p zone. Under illumination, the photogenerated electrons and holes will move oppositely driven by the internal electrical field and separate from each other.

Fast separation of photogenerated electron-hole pairs is essential but not sufficient to achieve high-performance photocatalysts. For example, it is important to transfer the separated electrons and holes to the surface of the photocatalyst quickly and timely, otherwise they would recombine instead of participating in reactions. A high electrical conductivity can facilitate the charge transportation. However, most semiconductors do not possess a satisfying electrical conductivity. In this consideration, combining semiconductors with highly conductive materials of large work function becomes the reasonable choice. Graphene, which possesses a conductivity of $20000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and large work function at room temperature [59], is an ideal material coupling with semiconductors to form the semiconductor-graphene heterojunction. Not only the high conductivity and large work function, its large specific surface area also can facilitate the photocatalytic activity. Benefitting from this type of heterojunction, the photogenerated electrons can

Fig. 4. Schematic illustration of the internal field of a PN heterojunction.

Fig. 5. (a) Band structure of Schottky heterojunction; (b) Illustration of the oscillation of electrons in a metal particle; (c) Harmonic model to describe the plasmon resonance.

be transferred quickly to and accumulate on the graphene surface, where redox reactions occur.

Combining a semiconductor with a metal can form the Schottky heterojunction. Usually, it is required that the metal's work function should be lower than the semiconductor's Fermi level. In this way, after contacting the metal with the semiconductor intimately, the electrons in the semiconductor would flow to the metal due to the lower Fermi level, leaving the positive ions. An electrical field is then formed pointing from the semiconductor to the metal, aligning the band of the semiconductor downwards until the Fermi level equals. The band structure of representative Schottky heterojunctions are shown in Fig. 5(a). Due to the band alignment of the contacting metal and semiconductor, an energy barrier is established with a barrier height determined by the difference of the corresponding work functions. The energy barrier steers the flow of charge carriers that are photogenerated in the semiconductor. The metal serves as a sink for the photogenerated electrons or holes when forming a Schottky junction with a n-type or p-type semiconductor, respectively. Under illumination, the Schottky barrier can prohibit the backflow of photogenerated electrons or holes from metal to semiconductor, achieving efficient unidirectional transfer of charge carriers across the interface and thus preventing the recombination of electron-hole pairs in the semiconductor. Other than the Schottky heterojunction, the combination with metals can also benefit the transportation of electrons to the surface for reactions. Combining with metals can additionally improve the light absorption, which is of equal

importance for the photocatalytic efficiency. Particularly, surface plasmon resonance (SPR) has been proposed to enhance the light absorption of photocatalysts. Surface plasmons are the collective movement of the free electrons in metals, as shown in Fig. 5(b) and (c). The surface plasmons act as oscillators interacting with driving electromagnetic waves. The excitation of surface plasmons could largely increase the light-absorption cross-section of the structure, thus promoting the light harvesting. In addition, the plasmonic effect can generate "hot electrons" that can participate in the redox reaction.

To summarize this section, the basic principle to build an efficient photocatalyst based on heterojunctions is to find the appropriate interactions that can separate the photogenerated electron-hole pairs. For example, in type II or Schottky heterojunctions, the flow of electrons/holes to lower energy levels is actually driven by the principle of minimum energy, or we can say the second law of thermodynamics. In PN heterojunction and S-scheme heterojunction, the interaction that separates the electrons and holes is the internal electric field. A table that summarizes the similarity and difference of various heterojunctions is shown in Table 1.

3. Construction of different types of heterojunctions

3.1. Type II heterojunctions

Tremendous efforts have been dedicated to the development of type II heterojunction photocatalysts due to their effectiveness to separate the photogenerated electron-hole pairs. Lots of type II heterojunctions were designed and prepared, such as WO_3/TiO_2 [60], NiO/TiO_2 [61], $\text{CsPbBrCl}_2/\text{g-C}_3\text{N}_4$ [62], CdS/ZnSe [63], $\text{SnO}_x/\text{Zn}_2\text{SnO}_4$ [64], $\text{CuSbSe}_2/\text{TiO}_2$ [65] and so on, as compared in Table 2.

Most recently, Wang et al. constructed a type II $\text{g-C}_3\text{N}_4/\text{ZnTe}$ heterojunction for the photosynthesis of ethanol by reducing CO_2 [68]. Usually, the reduction of CO_2 to ethanol (a C_2 product) is limited due to the rate-limiting step of C–C coupling. ZnTe is a promising photocatalytic material with high selectivity of reducing CO_2 to CO , while $\text{g-C}_3\text{N}_4$ can facilitate the C_2 production because of the abundant pyridinic N sites, which are crucial for CO^* dimerization and ethanol formation. By the combination of ZnTe and $\text{g-C}_3\text{N}_4$, the authors reported an impressive ethanol generation rate of $17.1 \mu\text{mol cm}^{-2} \text{h}^{-1}$ at -1.1 V vs. Ag/AgCl , which is much better than that of separated $\text{g-C}_3\text{N}_4$ and ZnTe (Fig. 6). The formation of the $\text{g-C}_3\text{N}_4/\text{ZnTe}$ heterojunction not only boosted the separation of photogenerated electron and holes, but also accelerated the transportation of electrons from ZnTe to $\text{g-C}_3\text{N}_4$ driving by the built internal field. The $\text{g-C}_3\text{N}_4/\text{ZnTe}$ -1-2 sample exhibits the highest $\text{C}_2\text{H}_5\text{OH}$ genera-

Table 1
Similarity and difference of various heterojunctions.

Heterojunctions	Similarity	Difference
Type II and S-scheme heterojunctions	Similar band alignment	Recombination pathway
Type II and PN heterojunctions	Similar charge separation pathway	The built-in field is against the charge separation for Type II heterojunction
PN and Schottky heterojunctions	Strong internal field	Schottky barrier is formed for Schottky heterojunction

Table 2

Comparison of some recently developed type II heterojunction photocatalysts.

Heterojunction	Application	Performance	Year	Ref.
WO ₃ /TiO ₂	Stearic acid degradation	14 times higher than pure TiO ₂	2017	[60]
NiO/TiO ₂	H ₂ generation	22 times greater than TiO ₂	2018	[61]
CsPbBrCl ₂ /g-C ₃ N ₄	Organic effluents degradation	Degrading 94% of Eosin B dye within 120 min	2019	[62]
CdS/ZnSe	Water splitting	Higher carrier mobility	2018	[63]
SnO _x /Zn ₂ SnO ₄	Degradation of methyl orange	Complete decolorization in 30 min	2017	[64]
CuSbSe ₂ /TiO ₂	Degradation of organic dyes	21.08% increase in the degradation efficiency than TiO ₂	2019	[65]
WO ₃ /BiOBr	Oxidation of amine to imine	2 times higher than WO ₃	2020	[66]
ZnO/Ag ₂ S	Anti-bacteria	Significant antibacterial activity	2020	[67]
g-C ₃ N ₄ /ZnTe	Photosynthesis of ethanol	Generation rate of 17.1 μmol cm ⁻² h ⁻¹ (at -1.1 V vs. Ag/AgCl)	2019	[68]
I-BiOCl/I-BiOBr	Degradation of methyl orange	7 times than BiOBr	2017	[69]
La ₂ Ti ₂ O ₇ /In ₂ S ₃	H ₂ generation	18 times higher than physical mixtures of La ₂ Ti ₂ O ₇ and In ₂ S ₃	2019	[70]
BiVO ₄ /WO ₃	Photoanode	2.15 times enhancement than WO ₃	2016	[71]
Pt/TiO ₂ /CdS/Co ₃ O ₄	H ₂ generation	A generation rate of 2000 μmol g ⁻¹ h ⁻¹	2018	[72]
VO ₂ /CuWO ₄	Degradation of azure II	Degrading 83.8% in 80 min	2018	[73]
ZnS/g-C ₃ N ₄	MB degradation	2.6 times better compared to bare g-C ₃ N ₄	2017	[74]
Cu ₂ O/g-C ₃ N ₄	H ₂ generation	4 times higher than pure g-C ₃ N ₄	2017	[75]
CuS/BiFeO ₃	Degradation of alachlor	95% degradation within 1 h	2018	[76]
Cu ₂ O/SnO ₂	RhB degradation	2-fold higher than individual SnO ₂	2016	[77]
S/CdS	H ₂ generation	8.14 mmol h ⁻¹	2017	[78]
Mn ₃ O ₄ /MnO ₂	MB degradation	93.5% degradation within 1 h	2017	[79]
SnS ₂ /H-TiO ₂ /Ti	H ₂ generation	70 times higher than SnS ₂ /TiO ₂ /Ti	2019	[80]
TiO ₂ /CdIn ₂ S ₄	H ₂ generation	5.5 times higher than bare TiO ₂	2018	[81]
IO/CdS	Degradation of xylenol blue	97.6% degradation within 3 h	2019	[82]
g-C ₃ N ₄ /P25	H ₂ generation	24.5 times higher than pure g-C ₃ N ₄	2019	[83]
ZnIn ₂ S ₄ /BiPO ₄	TC degradation	84% degradation within 80 min	2019	[84]
Bi ₂ SiO ₅ /BiPO ₄	Phenol degradation	4.36 times higher than Bi ₂ SiO ₅	2018	[85]
g-C ₃ N ₄ /Nb ₂ O ₅	RhB degradation	9.4 times higher than Nb ₂ O ₅	2017	[86]

tion rate, along with considerable amount of side product of C₃H₇OH. Further optimization of the mass ratio of g-C₃N₄ to ZnTe may improve the ethanol selectivity.

Jia et al. [69] proposed a novel strategy to transform type I heterojunction into type II heterojunction. BiOCl/BiOBr is originally a type I heterojunction material, which is not suitable for the separation of photogenerated charges. The authors used I-ions as dopants to raise the valence band positions of BiOCl and BiOBr, respectively. The rise of valence band can narrow the bandgap, resulting in more efficient light energy usage. Furthermore, the valence band position of BiOX (X = Cl, Br) can be controlled by the doping amount of I-ions. Applying this strategy, the valence band position of I-BiOBr was successfully aligned below that of I-BiOCl, reforming the type-II I-BiOCl/I-BiOBr heterojunction (Fig. 7(a)). Several samples with various molar percentage ratios of I-BiOCl to I-BiOBr were prepared and their photocatalytic activity measurements for methyl orange (MO) and phenol removal were carried out. It is found that all the I-BiOCl/I-BiOBr composites exhibited remarkable photocatalytic activity, while the 20% I-BiOCl sample performs the best, as shown in Fig. 7(b) and (d). The pseudo-first-order rate constant was calculated to analyze the reaction kinetics of MO and phenol degradations, with results shown in Fig. 7(c) and (e). The 20% I-BiOCl sample possesses the highest kinetics, which accounts the best degradation performance. The doping method, however, could change the inherent properties of the material somehow. The rational con-

Fig. 6. (a) HRTEM image of g-C₃N₄/ZnTe. (b) Products of g-C₃N₄/ZnTe-*x-y* (*x* and *y* represented the mass ratio of g-C₃N₄ and ZnTe at -1.1 V vs. Ag/AgCl). (c) Products of g-C₃N₄/ZnTe-1-2 at various applied potentials. (d, e) The optimized geometry structures and binding energies for CO₂ (d) and CO (e) adsorption on g-C₃N₄, ZnTe, and g-C₃N₄/ZnTe. (f) Schematic diagram of band configuration and the charge separation at the interface of g-C₃N₄/ZnTe heterojunction. (reproduced with permission [68], copyright 2019, Elsevier).

Fig. 7. (a) Band structure of type-II I-BiOCl/I-BiOBr composite. Photocatalytic activities (b,d) and corresponding k_{app} constant (c,e) of various samples for MO and phenol degradation. (reproduced with permission [69], copyright 2017, Elsevier).

trol of doping type and amount of materials is of vital importance.

Material with multiple type II heterojunctions are also investigated. For example, Tang et al. [87] fabricated a triadic QD@LDH@BiVO₄ (QD: CdTe quantum dots, LDH: Co-based layered double hydroxide) photoanode to highly enhance the photoelectrochemical water oxidation efficiency. The photoanode possesses two sets of consecutive Type-II band alignments, the QD@LDH and the LDH@BiVO₄, as shown in Fig. 8(a). To highlight the photocatalytic performance of this special material, BiVO₄ without a type II heterojunction structure, and LDH@BiVO₄ with one type II heterojunction structure, were also prepared and their photoactive performance was measured and compared. Experimental results revealed that the photocurrent and the IPCE (incident-photon-to-current conversion efficiency) of QD@LDH@BiVO₄ is two times that of LDH@BiVO₄. The water oxidation efficiency of QD@LDH@BiVO₄ reaches above 90% at a low potential of 0.5 V vs RHE, which is superior to most BiVO₄-based materials. The outstanding performance is proved to be attributed to the unique band configuration with two consecutive type II band alignments between the ternary components, which greatly improves electron transfer and hole diffusion.

In the past decade, the adoption of 2D materials also appealed particular interest in the field of photocatalysis, due to

Fig. 8. (a) Band alignment of the QD@LDH@BiVO₄ (QD: CdTe quantum dots, LDH: Co-based layered double hydroxide) photoanode. (b–d) SEM images of BiVO₄, LDH@BiVO₄ and QD@LDH@BiVO₄, respectively. (e) HRTEM images of QD@LDH@BiVO₄. (f) Oxidation efficiency of the surface-reaching holes injected into the solution species. (reproduced with permission [87], copyright 2016, American Chemistry Society).

their exotic electrical or optical properties. Because of the 2D nature, they can minimize the distance that photogenerated electrons and holes have to travel until to the surface for redox reactions. Type II heterojunctions based on 2D materials have been designed and studied as efficient photocatalysts theoretically or experimentally [70,88–90]. For example, Kumar et al. [88] designed C₂N/WS₂ heterojunction (Fig. 9) theoretically. The heterojunction could facilitate water splitting in three aspects. First, the band gap reduces due to the compounding of the constituent monolayers, enhancing significantly the light absorption. Second, the band edges of the heterostructure satisfies both water oxidation and reduction potential levels.

Fig. 9. (a,b) Top and side view of the C₂N/WS₂ heterojunction. Grey, green, purple and orange colors denote C, N, W and S atoms, respectively. (c) Band structure of the C₂N/WS₂ heterojunction. (d) Absolute energy positions of VBM (valence band maxima) and CBM (conduction band minima) for all three structures with respect to vacuum level. (reproduced with permission [88], copyright 2018, Elsevier).

Third, the band structure of the heterojunction forms a type-II alignment, enabling the transportation of electrons and holes into different C_2N and WS_2 layers respectively, which prevents the recombination efficiently. In another work, Hua et al. fabricated experimentally a 2D type-II heterojunction $La_2Ti_2O_7/In_2S_3$ [70] (Fig. 10). Firmly intimate contact of the two layers was realized because of the strong coulomb static force between $La_2Ti_2O_7$ and In_2S_3 due to their inverse Zeta potentials. The strong interaction between the two layers and the type II band structure co-promoted the charge separation, which accounts for the superior photocatalytic activity for hydrogen production. Various heterojunctions with different mass ratios of $La_2Ti_2O_7$ to In_2S_3 were prepared and measured. Experimental results revealed an optimal mass ratio at 7.5:1.0, where the sample demonstrated a hydrogen production rate 3.5 times higher than pristine In_2S_3 and 18 times higher than physical mixtures of $La_2Ti_2O_7$ and In_2S_3 .

3.2. PN heterojunctions

Although type II heterojunctions can separate photoinduced charges with a high efficiency, it was reported that PN heterojunctions can separate the charges even faster [91], with the aid of internal electric fields. Therefore, PN heterojunctions belong to an important branch of heterojunction-based photocatalysts. Numerous PN heterojunctions have been fabricated and studied, with recent works like $Ag_2O/Bi_2O_2CO_3$ [92], $Fe_2O_3/BiOI$ [93], $Cu_3P/g-C_3N_4$ [94], $MoSe_2/Bi_2WO_6$ [95], $ZnO/MnWO_4$ [96], $BiOI/BiPO_4$ [97], Cu_2O/SnO_2 [98] and so on. The performance

Fig. 10. (a) TEM image of the $La_2Ti_2O_7/In_2S_3$ heterojunction. (b) HRTEM image of the $La_2Ti_2O_7/In_2S_3$ heterojunction. (c) Schematic illustration of the band edge positions for both $La_2Ti_2O_7$ and In_2S_3 . (reproduced with permission [70], copyright 2019, Elsevier).

of some PN heterojunction photocatalysts are listed in Table 3.

Most recently, Liu et al. [118] prepared the $Cu_{2-x}Se/CdS$ PN heterojunction composite to improve the degradation rate of Rhodamine B (RhB). $Cu_{2-x}Se$ is a p type semiconductor while CdS is an n type one (Fig. 11). When the two semiconductors

Table 3

Comparison of some recently developed PN heterojunction photocatalysts.

Heterojunction	Application	Performance	Year	Ref.
$Fe_2O_3/BiOI$	RhB degradation	4.24 times higher than single BiOI	2016	[93]
$Cu_3P/g-C_3N_4$	Hydrogen generation	95 times higher activity than bare $g-C_3N_4$	2018	[94]
$MoSe_2/Bi_2WO_6$	Degradation of gas-phase toluene	7 times higher compared with pure $MoSe_2$	2018	[95]
$ZnO/MnWO_4$	Degradations of RhB, MB, MO	22.5, 17.7, 26.8 times higher than that of the ZnO sample in degradations of RhB, MB, MO	2018	[96]
$BiOI/BiPO_4$	Degradation of tetracycline	1.98 times and 2.46 times higher than BiOI and $BiPO_4$	2019	[97]
$Ag_2S/BiVO_4$	Degradation of tetracycline	90.2% degradation efficiency	2019	[99]
$Ag_2O/AgNbO_3$	Degradation of RhB	Degradation efficiency of 95.4% within 90 min	2019	[100]
$MoS_2/MgIn_2S_4$	NH_3 production	4 and 7 times higher than bare MoS_2 and $MgIn_2S_4$	2020	[101]
Bi_2O_3/MoS_2	Hydrogen generation	10 times higher than pure Bi_2O_3 and MoS_2	2020	[102]
$ZnFe_2O_4/SnS_2$	Degradation of MO	1.7 times higher than individual $ZnFe_2O_4$	2020	[103]
$BiVO_4@MoS_2$	Reduction of Cr^{6+}	76.5 % Cr^{6+} reduced within 90 min	2016	[104]
$g-C_3N_4/Bi_4Ti_3O_{12}$	Degradation of acid orange-II	2.85 times higher than pure $Bi_4Ti_3O_{12}$	2016	[105]
$WO_6/BiOI$	Antifouling	99.99% <i>P. aeruginosa</i> , <i>E. coli</i> and <i>S. aureus</i> killed within 60 min	2016	[106]
$BiPO_4/BiOCl$	MO degradation	A degradation efficiency of 98% within 14 min	2015	[107]
Ag_2O/Bi_5O_7I	Degradation of Bisphenol A and phenol	A degradation efficiency of 99.9% within 40 min	2017	[108]
$BiOI/CeO_2$	MO degradation	A degradation efficiency of 93.75% within 50 min	2017	[109]
Ag_2O/TiO_2	PNP degradation	7.7 times higher than TiO_2	2015	[110]
$CdWO_4/BiOBr$	Degradation of RhB	2.8 times better than BiOBr	2016	[111]
$BiPO_4/BiOBr$	<i>o</i> -Dichlorobenzene removal	A removal efficiency of 53.6%	2017	[112]
CuO/ZnO	Degradation of RhB and CR	Complete degradation within 60 min	2017	[113]
$Ag_2O/BiOCCOOH$	Degradation of RhB	96.8% degradation within 60 min	2017	[114]
$Bi_2Sn_2O_7/Ag_2CrO_4$	Degradation of RhB, MO and MB	97.5%, 90.4% and 99.8% degradation within 120 min, respectively	2018	[115]
$Co_3O_4/Bi_2O_2CO_3$	Degradation of MO	90% degradation within 150 min	2017	[116]
$BiOI/TiO_2$	Selective hydroxylation of phenol	A selectivity of 92.1%	2018	[117]

Fig. 11. (a) The charge transfer pathway between Cu_{2-x}Se and CdS under illumination. (b,c) SEM and TEM images of 10 wt% $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ composite. (d) Photocatalytic performance of CdS and different ratios of $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ composites. (reproduced with permission [118], copyright 2019, Elsevier).

hybrid, an internal electric field is established pointing from CdS to the Cu_{2-x}Se side. Samples with various mass ratios of Cu_{2-x}Se were prepared. It was found that the 10 wt% $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ composite performed the best in RhB degradation process with a superior rate, which was almost 8 times higher than that of pure CdS . Further analysis revealed that the boosted photocatalytic efficiency could be mainly ascribed to the formation of a PN heterojunction at the interface of $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ material, which accelerated the charge separation and thus reduced the recombination possibility in the photocatalyst. In this work, the $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ heterojunction was prepared by facile a hydrothermal method. It is expected that the interaction between Cu_{2-x}Se and CdS could be improved by optimizing the preparation process, which may yield stronger internal field and higher efficiency.

Lu et al. [119] proposed a strategy that PN heterojunction could be constructed through a phase transition method. In this work, $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ photocatalysts were prepared by a facile one-step calcination process. Specifically, $\alpha\text{-Bi}_2\text{O}_3$ can be obtained by keeping $\text{Bi}(\text{NO}_3)_3$ powder at a temperature of 600 °C for 4 h. However, if nano-sized SiO_2 powder was mixed to the $\text{Bi}(\text{NO}_3)_3$ powder, $\alpha\text{-Bi}_2\text{O}_3$ would transform to its counterpart phase $\beta\text{-Bi}_2\text{O}_3$ under the same calcination condition (Fig. 12). Also, Bi_2SiO_5 were generated with the addition of nano-sized SiO_2 powder. The emergence of the usual metastable $\beta\text{-Bi}_2\text{O}_3$ can be attributed to the suppression of heat release of $\text{Bi}(\text{NO}_3)_3$, due to the formation of Bi_2SiO_5 coated on the surface. Typically, Bi_2SiO_5 is an n type semiconductor while $\beta\text{-Bi}_2\text{O}_3$ is p-type one. Thus, their combination resulted in the formation of a PN heterojunction, which drove the separation of photogenerated electrons and holes. Therefore, with the enhanced charge separation, the larger specific surface area and the improved light response range, the $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction exhibited great enhancement of photocatalytic activity compared to $\alpha\text{-Bi}_2\text{O}_3$.

Novel 2D/2D PN heterojunctions were also synthesized. For

example, Ao et al. [120] prepared a 2D/2D $\text{BiOBr}/\text{La}_2\text{Ti}_2\text{O}_7$ photocatalyst to enhance the photocatalytic degradation of Rhodamine B and phenol under both UV and visible light irradiation. BiOBr can be excited by both UV and visible light, while $\text{La}_2\text{Ti}_2\text{O}_7$ can be excited only by UV light due to the larger bandgap. In this work, lamellar $\text{La}_2\text{Ti}_2\text{O}_7$ were first prepared by a hydrothermal method. Then, smaller BiOBr nanoplates were dispersed on the larger $\text{La}_2\text{Ti}_2\text{O}_7$ nanosheets through a simple an in-situ growth method (Fig. 13(a)). Thus, tremendous PN heterojunctions were formed at the interfaces of the two 2D materials, which not only accelerated the photogenerated electrons to transfer to $\text{La}_2\text{Ti}_2\text{O}_7$ under visible light, but also accelerated the holes to transfer to BiOBr under UV light. Consequently, the $\text{BiOBr}/\text{La}_2\text{Ti}_2\text{O}_7$ compound could decompose contaminants much faster compared to pristine $\text{La}_2\text{Ti}_2\text{O}_7$.

3.3. Schottky heterojunctions

Photocatalysts based on semiconductor/metal Schottky heterojunctions have been proposed and prepared by different groups [121–134], with typical examples shown in Table 4. Recently, Zhong et al. [135] constructed a CdS/Cd Schottky junction photocatalyst to facilitate the hydrogen production from water splitting. Ultrafast laser technique was adopted to fabricate the novel material. Specifically, metallic Cd clusters could be generated in situ on the surface of CdS after the laser treatment, forming the Schottky heterojunction (Fig. 14). Due to the generation of Cd clusters, the photocatalytic hydrogen yield of CdS/Cd was 40 times compared to that of pure CdS in

Fig. 12. (a) The schematic transformation from $\alpha\text{-Bi}_2\text{O}_3$ to the $\beta\text{-Bi}_2\text{O}_3$. (b,c) TEM and HRTEM images of $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction. (d) Photocurrent responses of $\alpha\text{-Bi}_2\text{O}_3$ and $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunctions. The products with the SiO_2 mass ratio of 1%, 5%, 10%, 15% and 20% were denoted as BiSi-1, BiSi-2, BiSi-3, BiSi-4 and BiSi-5, respectively. (reproduced with permission [119], copyright 2018, Elsevier).

Fig. 13. (a,b) TEM and HRTEM images of the BiOBr/La₂Ti₂O₇ heterojunction. (c) Photocatalytic activity of various samples for RhB degradation. (d) Schematic diagram of the possible photocatalytic mechanism over BiOBr/La₂Ti₂O₇ under both UV and visible light irradiation. (reproduced with permission [120], copyright 2016, Elsevier).

four hours. The improved performance was attributed to three aspects. First, the Cd clusters served as electron skins to accept the excited electrons via the Schottky heterojunction. Second, the CdS/Cd exhibited stronger adsorption capacity for sacrificial agents, promoting the consumption of holes. Third, the

narrowed band gap benefited much stronger light absorption. Although the pulse laser induced the Schottky heterojunctions, the yield of Cd clusters is relatively low. Operations that improve the yield of Cd clusters, such as larger optical power, are expected to further improve the photocatalytic performance.

Gu et al. [125] designed dual RuO₂/TiO₂ type II heterojunction and Ru/TiO₂ Schottky heterojunction to enhance the photocatalytic full water splitting. TiO₂ nanobelts (NBs) were modified with metallic Ru and RuO₂ nanoparticles through a wet-impregnation reduction method, as illustrated in Fig. 15. The band structure analysis revealed the formation of a Schottky junction at the Ru/TiO₂ interface and a type II heterojunction at the RuO₂/TiO₂ interface. The RuO₂/TiO₂ heterojunction can improve the transfer of the photogenerated holes from TiO₂ to RuO₂ to produce O₂, while the Ru/TiO₂ Schottky heterojunction can promote the transfer of photogenerated electrons from TiO₂ NBs to the Ru for proton reduction into H₂.

In addition to the formation of the Schottky heterojunction, the combination of a semiconductor and a metal could also benefit from the plasmon effect with proper metal size [149–152]. Xiao et al. [153] prepared metal-organic framework (MOF) composites to enhance the photocatalytic activity by Integrating plasmonic effects and Schottky junctions. Utilizing a semiconductor-like MOF MIL-125, a Pt@MIL-125/Au catalyst was prepared, which integrated the surface plasmon effect of Au nanorods with a Pt/MOF Schottky heterojunction. The plasmonic excitation effectively extended the light absorption

Table 4

Comparison of some recently developed Schottky heterojunction photocatalysts.

Heterojunction	Application	Performance	Year	Ref.
Ru/TiO ₂	Water splitting	H ₂ evolution rate of 40.2 μmol h ⁻¹ g ⁻¹	2016	[125]
Au/Cu ₂ O	MO degradation	1.2 times higher than pure Cu ₂ O microcubes	2016	[127]
TiO ₂ /NC-Ru	Oxidation of benzyl alcohol	99% selectivity	2019	[128]
TaON/Ni	Reduction of CO ₂ to CH ₄	5.1 times higher than pristine TaON	2019	[129]
Bi ₂ MoO ₆ /Ti ₃ C ₂	Molecular oxygen activation	5.6 times higher than pristine samples	2020	[130]
CoSe ₂ /CdS _{0.95} Se _{0.05}	H ₂ evolution	66 times higher than CdS	2020	[131]
Co _{1.4} Ni _{0.6} P	H ₂ evolution	H ₂ evolution rate of 405 μmol h ⁻¹ g ⁻¹	2020	[132]
PdAg/g-C ₃ N ₄	Dehydrogenation of formic acid	TOF of 420 h ⁻¹	2019	[133]
CdS/Ti ₃ C ₂	H ₂ evolution	7 times higher than CdS	2020	[134]
CdS/Cd	H ₂ evolution	40 times compared to pure CdS	2019	[135]
Pd/SiC	Coupling of iodobenzene and phenylboronic acid	A high turnover frequency of 1053 h ⁻¹ and a selectivity of nearly 100%	2015	[126]
Ag/Ag ₂ O	MO degradation	84%, 78% and 88% of MO are degraded under UV, visible and NIR irradiation	2016	[136]
CoP/g-C ₃ N ₄	H ₂ evolution	The 2D/2D structure performs 2.1 times better than 0D/2D structure	2018	[137]
Ru/TiO ₂	Aerobic oxidation of benzyl alcohol	84% of MO degraded for 25 min	2016	[138]
Ag/CeO ₂	MB degradation	95.33% of MB degraded within 30 min	2015	[139]
Pd/BiFeO ₃	MO degradation	10.7 times higher than BiFeO ₃	2016	[140]
CQDs/H-γ-TaON	H ₂ evolution	H ₂ evolution rate of 496.5 μmol h ⁻¹	2015	[141]
1T-MoS ₂ /CdS	H ₂ evolution	39 times higher than pure CdS	2016	[142]
CdS/Cd	H ₂ evolution	H ₂ evolution rate of 1.68 mmol h ⁻¹	2015	[31]
1T-MoS ₂ /O-g-C ₃ N ₄ 2D	H ₂ evolution	H ₂ evolution rate of 1841.72 μmol h ⁻¹ g ⁻¹	2018	[143]
Ni/NiTe ₂	H ₂ evolution	A rate of 2214.2 μmol g ⁻¹ h ⁻¹	2020	[144]
Ag/CN	H ₂ evolution	H ₂ evolution rate of 364.6 μmol g ⁻¹	2019	[145]
Ag ₂ WO ₄ /Ti ₃ C ₂	Degradation of TC and SFE	Degradation rate of 62.9% and 88.6%, respectively	2019	[146]
Bi/Bi ₂ O ₂ CO ₃	MB degradation	Complete degradation within 60 min	2016	[147]
Pt/PbS	H ₂ evolution	14.38 times higher than PbS	2017	[148]

Fig. 14. (a) A schematic of the generation of CdS/Cd Schottky junction. (b) Mechanism of the improved photocatalytic activity for CdS/Cd. (c) TEM image of CdS/Cd viewed from the [100] direction. (d,e) Enlarged view of the corresponding areas in (c). (f) Comparison of the photocatalytic hydrogen evolution over CdS and CdS/Cd. (g) Cycling hydrogen evolution measurements for CdS/Cd. (reproduced with permission [135], copyright 2019, Elsevier).

Fig. 15. (A) Illustration of the structure of Ru/TiO₂/RuO₂ heterojunctions. (B) Band structure of the Ru/TiO₂/RuO₂ heterojunctions. (C,D,E,F) TEM and HRTEM images of the Ru/TiO₂/RuO₂ heterojunctions. (G,H) Photocatalytic H₂ and O₂ evolution over Ru_{8.0}/TiO₂ NBS-T, where T indicates the annealing temperature. (reproduced with permission [125], copyright 2016, Wiley).

range of the MOF, while the Schottky heterojunction greatly accelerated the charge separation. Furthermore, to distinguish the great significance of the spatial position of Pt nanoparticles, the Pt/MIL-125/Au and MIL-125/Au samples were also prepared as references (Fig. 16). Interestingly, due to the spatial separation of Pt nanoparticles and Au nanorods by MIL-125, the sample Pt@MIL-125/Au demonstrated much better separation efficiency and lower charge transfer resistance than Pt/MIL-125/Au, where Pt nanoparticles and Au nanorods were co-dispersed on the MIL-125 surface. As a result, the

Pt@MIL-125/Au performed far more efficiently for photocatalytic hydrogen production than Pt/MOF/Au and MOF/Au. Large amount of noble metals was adopted in this work. To reduce the expenditure, other plasmonic metals such as Al or Cu could be considered as substitutes.

3.4. S-scheme heterojunctions

To fully exploit the reduction/oxidation ability of the photogenerated electrons/holes, the S-scheme heterojunctions are proposed and prepared very recently based on previous studies of heterojunction photocatalysts [154–163]. Due to the band similarity, the recombination mechanism in S-scheme heterojunctions should be carefully verified to distinguish the S-scheme from the type II heterojunctions. Rational theoretical calculations combined with powerful characterization techniques could be a convinced way to confirm the S-scheme mechanism. Particularly, theoretical calculations such as density functional theory simulations help to determine the work functions of various semiconductors and charge distributions at the heterojunction interface, and thus the internal electric field at the interface. Further, in situ irradiated X-ray photoelectron spectroscopy (XPS) measurement could observe the electron flow direction at the heterojunction interface before and after light irradiation. In addition, electron paramagnetic resonance (EPR) spectrum could detect the redox radicals with specific reaction potentials, such as $\cdot\text{OH}$ or $\cdot\text{O}_2^-$, which helps to determine the oxidation and reduction sites located in different parts of the heterojunction. Finally, a S-scheme charge transfer pathway could be confirmed with photoinduced electrons and holes accumulated in the semiconductor of more negative CB and the semiconductor of more positive VB, respectively. Some S-scheme heterojunction photocatalysts are compared in Table 5.

For instance, Xia et al. [177] designed a 0D/2D S-scheme heterojunction of CeO₂/PCN (polymeric carbon nitride) for the

Fig. 16. (a) Schematic illustration showing the synthesis of Pt@MIL-125/Au and the corresponding Pt/MIL-125/Au and MIL-125/Au analogues. (b) Photocatalytic H₂ production rates of different catalysts. (c) Schematic illustration showing the electron migration at the two metal/MOF interfaces. (reproduced with permission [153], copyright 2018, Wiley).

Table 5

Comparison of some recently developed S-Scheme heterojunction photocatalysts.

Heterojunction	Application	Performance	Year	Ref.
V ₂ O ₅ /g-C ₃ N ₄	RhB degradation	7.3 and 13.0 times higher than individual g-C ₃ N ₄ and V ₂ O ₅	2016	[154]
Bi ₂ Fe ₄ O ₉ /Bi ₂ WO ₆	RhB degradation	Complete degradation within 90 min	2018	[155]
Ag ₂ CrO ₄ /GO	MB degradation	3.5 times higher than Ag ₂ CrO ₄	2015	[156]
TiO ₂ /CdS	CO ₂ reduction	3.5 and 5.4 times higher than CdS and TiO ₂	2019	[157]
BP/Bi ₂ WO ₆	H ₂ generation	9.15 times that of pristine	2019	[158]
ZnO/CeO ₂	RhB degradation	2.5 and 1.7 times than pristine ZnO and CeO ₂	2018	[159]
CdS/ α -Fe ₂ O ₃	H ₂ generation	H ₂ production rate of 45 mmol h ⁻¹ g ⁻¹ and high quantum efficiency of 46.9%	2020	[160]
CdS/g-C ₃ N ₄	H ₂ generation	H ₂ production rate of 15.3 mmol g ⁻¹ h ⁻¹	2020	[161]
WO ₃ (H ₂ O) _{0.333} /Ag ₃ PO ₄	MB degradation	Complete degradation in 4 min	2019	[162]
g-C ₃ N ₄ /C-TiO ₂	RhB degradation	150 times higher than TiO ₂	2019	[163]
WO ₃ /g-C ₃ N ₄	H ₂ generation	H ₂ production rate of 982 μ mol h ⁻¹ g ⁻¹	2019	[58]
g-C ₃ N ₄ /Ag ₃ VO ₄	MB degradation	Degradation rate of 99.3% within 8 min	2019	[164]
SnFe ₂ O ₄ /ZnFe ₂ O ₄	Tetracycline degradation	93.2% removal efficiency	2020	[165]
Ni ₂ P-SNO/CdS-D	Hydrogen production	Hydrogen production rate of 7808 μ mol g ⁻¹ h ⁻¹	2020	[166]
BiOBr/Bi ₂ MoO ₆	Degradation of RhB	66.7% total organic carbon could be removed	2017	[167]
Bi ₂ S ₃ /Pg-C ₃ N ₄	MB degradation	29.74 times greater than Bi ₂ S ₃	2019	[168]
g-C ₃ N ₄ /SnS ₂	CO ₂ reduction	CH ₃ OH yield of 2.3 μ mol g ⁻¹ and CH ₄ yield of 0.64 μ mol g ⁻¹	2017	[169]
WO ₃ /g-C ₃ N ₄	TC degradation	Degradation rate of 90.54% within 120 min	2020	[170]
Pg-C ₃ N ₄ /Zn _{0.2} Cd _{0.8} S	H ₂ generation	hydrogen production rate of 6.69 mmol g ⁻¹ h ⁻¹	2020	[171]
Ag ₃ VO ₄ /BiVO ₄	Photocatalytic reduction of Cr ⁶⁺ and oxidation of Bisphenol S	Photocatalytic reduction and oxidation efficiency of 74.9% and 94.8%	2019	[172]
LaCoO ₃ /g-C ₃ N ₄	Phenol degradation	7.5 times higher than g-C ₃ N ₄	2019	[173]
Cd _{0.5} Zn _{0.5} S/g-C ₃ N ₄	Dye degradation	13 times higher than g-C ₃ N ₄	2020	[174]
NiO/BiOI	RhB degradation	8 times higher than NiO	2020	[175]
Bi ₂ S ₃ /BiFeO ₃	TC degradation	6 times higher than Bi ₂ S ₃	2020	[176]

sterilization towards *Staphylococcus Aureus*. Utilizing the wet chemistry method with following heat treatment, CeO₂ quantum dots were decorated on the PCN nanosheets uniformly without any usage of complicated organic solvent (Fig. 17). The 0D/2D configuration reduces effectively the diffusion length of photogenerated charges, while the large surface area of PCN nanosheets provide abundant sites to immobilize CeO₂ quan-

tum dots. Furthermore, due to the formation of S-scheme heterojunction, the CeO₂/PCN composite not only exhibited much higher charge separation efficiency than CeO₂ or PCN, but also preserved full redox ability. As a result, this novel material shows high photocatalytic anti-bacteria efficiency, with a sterilization rate of 88.1%, which is 2.7 and 8.2 times that of pure CeO₂ (32.2%) and PCN (10.7%), respectively.

Fig. 17. (a) TEM image of PCN nanosheets. (b) TEM image of the CeO₂/PCN heterojunction photocatalyst. Inset: corresponding HRTEM image of (111) plane of CeO₂. (c) HAADF-TEM image of the CeO₂/PCN heterojunction photocatalyst. (d) Band structure of pure CeO₂ and PCN. (e) The statistic counts of bacteria colonies treated with different samples, respectively. (f) The bacteria removal efficiency over the prepared samples. (reproduced with permission [177], copyright 2020, Wiley).

One-dimensional nanostructure is also a promising morphology for high-efficient photocatalysis. Ge et al. [178] fabricated S-scheme TiO_2/CdS composite nanofibers to facilitate the photocatalytic H_2 production. The well-distributed TiO_2/CdS nanofibers were prepared through a one-pot in situ method, where electrospinning and following low-temperature solid-phase synthesis were included. The TiO_2/CdS composites showed excellent photocatalytic H_2 production activities compared to pure TiO_2 and CdS (Fig. 18). Concretely, the sample TC10 exhibited the best activity with an apparent quantum efficiency of 10.14%, which outperforms most of its counterparts. This outstanding performance can be attributed to the formation of S-scheme heterojunction, which drives the photogenerated electrons to transfer toward CdS to consume the photogenerated holes in TiO_2 , leaving net electrons with higher reduction potential. The S-scheme recombination mechanism is verified by the EPR spectrum of TC10, where the signal of $\cdot\text{OH}$ radicals are observed. Otherwise, the holes in the VB of TiO_2 will migrate to that of CdS , the energy level of which is not enough to produce $\cdot\text{OH}$, eliminating its EPR signal.

Black phosphorus (BP) has been regarded as an emerging material for photocatalysis. Li et al. [179] coupled exfoliated BP with BiOBr nanosheets to construct a novel layered BP/BiOBr heterojunction photocatalyst for tetracycline (TC) removal and oxygen evolution. Through a facile solvothermal method, BiOBr nanosheets were self-assembled on the BP surface with intimate interfacial contact (Fig. 19). This S-scheme heterojunction created favorable conditions for the rapid separation and

transfer of photogenerated electron-hole pairs and retained the useful electrons and holes with higher redox potential. As a result, the unique BP/BiOBr sample yields superior photocatalytic performance, including an apparent reaction rate constant of 0.021 min^{-1} for TC degradation and a O_2 evolution rate of $89.5 \mu\text{mol g}^{-1} \text{ h}^{-1}$, which is 7.8 and 7.0 times than that of pure BiOBr , respectively. The oxygen evolution reaction potential is more positive than the VB position of BP, which indicates the oxygen evolution can only take place at the VB of BiOBr through the S-scheme charge transfer pathway. It is noted that the BP in this work presents a morphology of nanosheets. A quantum dot morphology may further improve the photocatalytic activity in consideration of larger contact area and more active sites.

Crystalline covalent organic frameworks (COFs), possessing large surface areas and tunable structures, offering abundant active sites, are expected to be promising building blocks for constructing highly efficient photocatalysts. Most recently, Zhang et al. [180] proposed a strategy to create organic/inorganic S-scheme photocatalysts for CO_2 reduction with H_2O as the electron donor. A systemic organic/inorganic COF/SCs (semiconductor) were prepared by condensation of COF precursors and hydroxyl-containing SCs (TiO_2 , Bi_2WO_6 , and $\alpha\text{-Fe}_2\text{O}_3$), as illustrated in Fig. 20(a), forming S-Scheme heterojunctions with COFs as the reduction catalyst and SCs as the oxidation catalyst, connected by covalent bonds. The COF/SCs samples exhibit outstanding photocatalytic activities. As shown in Figs. 20(b) and (c), COF-318/ TiO_2 displays an op-

Fig. 18. (a,b) TEM and HRTEM images of the TiO_2/CdS nanofiber. (c) Comparison of photocatalytic H_2 -production activity of T, TC5, TC10, TC20, and C samples. TCx: T and C represent TiO_2 and CdS , respectively, x indicates the weight percentage of CdS with respect to TiO_2 . (d) Cycling H_2 -production stability for the TC10 sample. (e) S-scheme charge separation and pathway in TiO_2/CdS nanofiber. (reproduced with permission [178], copyright 2019, Wiley).

Fig. 19. (a,b,c) SEM, TEM and HRTEM images of BP/BiOBr photocatalyst. (d) Photocatalytic degradation efficiency of tetracycline (TC) over various samples. (e) Photocatalytic oxygen evolution rate of various samples. (f) Schematic illustration for the charge transfer and reaction mechanism. BP: Black phosphorus. xBP/BiOBr : x indicates the weight ratio of BP respect to BiOBr . (reproduced with permission [179], copyright 2020, Elsevier).

Fig. 20. (a) Schematic illustration of the preparation of COF/SC photocatalysts. (b,c) Photocatalytic performance of the prepared COF/SC samples. (d) Schematic charge separation in COF/SC with COF-138/TiO₂ as an example. (reproduced with permission [180], copyright 2020, Wiley).

timel CO formation rate of 278.7 $\mu\text{mol g}^{-1}$, which is one of the highest values among CO₂ reduction photocatalysts, much better than pristine COF-318 and TiO₂. The enhanced performance is attributed to the efficient electron transfer from TiO₂ to COF-318 and the formation of S-Scheme heterojunction, which is reflected by the comparison of electrochemical potentials shown in Fig. 20(d), where the CB position of TiO₂ and the VB position of COF-138 exhibit very close levels with reference to the corresponding redox potentials of CO/CO₂ and O₂/H₂O reactions, respectively.

3.5. Surface heterojunctions

The atom arrangement and density could be different between different facets of a crystal. As a result, the electron movement and band structure on different facets may be diverse, which enables the possibility to design a heterojunction on a single semiconductor, namely the surface heterojunction. TiO₂ and BiVO₄ are the most-studied materials to construct a surface heterojunction [181–192]. For example, Liu et al. [188] prepared various TiO₂ surface heterojunctions with different (101)/(001) ratios by controlling the morphology of the TiO₂ crystal. Truncated octahedral bipyramid TiO₂ nanocrystals were synthesized in a solution system consisting of titanium butoxide, water, and hydrofluoric acid (HF). Interestingly, the morphology and thus the facet exposure percentage could be precisely controlled by adjusting the HF/H₂O ratio. The relative band position of (001) facets and (101) facets was shown in Fig. 21, matching a type II band alignment. Thus, the electrons transfer from (001) to (101) facets and holes transfer the other way around were facilitated due to the formation of the surface heterojunction. Moreover, the ratio of (101) to (001) were optimized to maximize the production of reactive oxygen species and the antibacterial activity. Experimental results revealed that the TiO₂ crystal with a ratio of 1.78 exhibited the best antibacterial performance, which was ascribed to the optimal activation of oxidative stress.

Rutile TiO₂ has not achieved photocatalytic activity comparable to that of anatase TiO₂ due to its higher recombination rate of electron-hole pairs. To obtain better photocatalytic activity of rutile TiO₂, Gao et al. [190] designed surface hetero-

junctions. As shown in Fig. 22, the fabrication of FH-TiO₂ (facet heterojunction) was achieved with a two-step hydrothermal method. First, rutile TiO₂ nanorods were grown on FTO substrate through the first hydrothermal step. Then, TiO₂ nanosheets were assembled on the TiO₂ nanorods through the second hydrothermal step, with special consideration on the reaction time, initial titanium precursor concentration, and temperature. TEM and XRD analysis reveals that the exposed dominant facet of the top portion of TiO₂ is the (101) facet, and the body portion is the (110) facet, forming countless (101)/(110) surface heterojunctions. The photocatalytic hydrogen evolution performance of the samples is displayed in Fig. 22(g), from which it can be seen the hydrogen evolution

Fig. 21. (a) Schematic illustration of the (101)/(001) surface heterojunction of TiO₂. (b) Schematic illustration of the adjustment of the facet ratio through morphology control. (c) SEM images of samples with different facet ratios. The (101)/(001) facet ratios of T1, T2, T3, and T4 were 49, 11.5, 1.78, and 0.087, respectively. (d,e) Bacterial viability of *E. coli* and *S. aureus* exposed to different concentrations of TiO₂ nanocrystals, respectively. (reproduced with permission [188], copyright 2017, American Chemical Society).

Fig. 22. (a,b) Schematic illustration of the formation of TiO₂ surface heterojunction. (c) Enlarged view showing the exposed facets of TiO₂. (d–f) SEM images of TiO₂ nanorods and TiO₂ nanorods loaded with nanosheets. (g) Photocatalytic performance of various samples. (h) Band alignment of the (111) and (101) facets of rutile TiO₂. FH-TiO₂: Facet Heterojunction TiO₂; TiO₂ nanorods loaded with nanosheets; P25: commercial TiO₂; NRs-anatase: nanorods with anatase phase; NRs-TiO₂: nanorods with rutile phase. (reproduced with permission [190], copyright 2019, Wiley).

rate of FH-TiO₂ is 45 times higher than pure rutile TiO₂. The underlying physics of enhanced performance can be understood as boosted charge separation due to the formation of surface heterojunctions, which drives the photogenerated electron transferring from (101) facets to (111) facets, the photo-generated holes from (111) facets to (101) facets.

Surface heterojunctions based on Bi-based semiconductors like BiVO₄ or BiOI were also constructed [196,197,204,205]. For instance, He et al. [205] reported surface heterojunctions based on BiOI, with enhanced photocatalytic activity for phenol degradation. Hierarchically structured BiOI were fabricated through a facile method including solid-state reaction and subsequent hydrolysis at room temperature (Fig. 23). To optimize the photocatalytic activity, the ratio of (110) to (001) facets was tuned by controlling the volume of water added in the hydrolysis. The different water volume created different pH environments, which played a key role in regulating the growth direction of BiOI nanoplates. Samples with various facet ratios were prepared and measured. BiOI-80 exhibited the best degradation performance, which was attributed to two factors. On one hand, the hierarchical structure of BiOI-80 enables strongest light absorption and offers the highest specific surface. On the other hand, the most surface heterojunctions are formed, which improves the separation of electrons and holes.

In short, some typical surface heterojunction photocatalysts are compared in Table 6.

3.6. Graphene-based heterojunctions

Tremendous heterojunction photocatalysts based on gra-

phene nanosheets have been developed due to their excellent electric conductivity, efficient charge separation ability and high surface areas [206,207]. Moreover, the diversity of graphene offers inexhaustible opportunities for the construction of heterojunction based photocatalysts. For example, the graphene exhibits amazing structural diversity, like 0D graphene quantum dots, 1D graphene nanoribbons, 2D graphene nanosheets and 3D graphene networks. The band structure and further the electrical or optical properties of graphene also show high tunability through the change of many factors like the number of layers, edge structure and the defect density [208], which enables graphene to form various types of heterojunctions with appropriate materials, such as type II heterojunction, S-scheme heterojunction, or Schottky heterojunction [209–223], as listed in Table 7.

Xia et al. [236] reported the combination of highly crystalline carbon nitride (CN) nanorods and graphene to form an ordered 2D/1D heterojunction (Fig. 24). The hybrid material exhibited excellent photocatalytic performance for the CO₂ reduction in the gas phase, in the absence of any cocatalyst or sacrificial agent. The loading amount of graphene was optimized to achieve best CO₂ conversion rate. Experimental results revealed that the best performance of graphene supported 1D nano-arrays of crystalline CNs could be 12.63 μmol h⁻¹ g⁻¹, which is 6 times and 4 times that of bulk CN and pure crystalline CN nanorods, respectively. The formation of unique 2D/1D heterojunction of graphene/CNs accounts for the enhanced photocatalytic performance, which improves light har-

Fig. 23. (a) SEM image of BiOI. (b,c) HRTEM images of BiOI viewed from the perpendicular and parallel directions of the BiOI plate, respectively. (d) Schematic illustration of the growth of BiOI nanoplate at different pH values. (e) Band alignment of (110) and (001) facet of BiOI. (f) Degradation curves of phenol on BiOI samples. BiOI-X: X means X mL distilled water was added in the hydrolysis process. (reproduced with permission [205], copyright 2016, Elsevier).

Table 6

Comparison of some recently developed surface heterojunction photocatalysts.

Heterojunction	Application	Performance	Year	Ref.
TiO ₂ (001)/(101)	H ₂ production	H ₂ evolution rate of 264 $\mu\text{mol h}^{-1}$	2016	[184]
TiO ₂ (001)/(101)	Reduction CO ₂ to CH ₄	CH ₄ production rate of 1.58 $\mu\text{mol h}^{-1} \text{g}^{-1}$	2016	[186]
TiO ₂ (001)/(101)	Removing Hg ⁰	87% Hg ⁰ removal efficiency	2017	[187]
TiO ₂ (001)/(101)	Anti-bacteria	50% decrease in the bacterial viability in 6 h	2017	[188]
Rutile TiO ₂ (111)/(101)	H ₂ production	0.566 $\text{mmol g}^{-1} \text{h}^{-1}$ H ₂ production rate in pure water	2019	[190]
18-facet SrTiO ₃ (001)/(110)	Water splitting	Fivefold enhancement of AQE than 6-facet SrTiO ₃	2016	[193]
ZnGa ₂ O ₄ (110)/(111)	H ₂ production	12.5 $\text{mmol g}^{-1} \text{h}^{-1}$ H ₂ production rate	2017	[194]
CaCu ₃ Ti ₄ O ₁₂ (001)/(111)	TC degradation	70 times higher than defect free CaCu ₃ Ti ₄ O ₁₂	2019	[195]
m-BiVO ₄ (010)/(110)	O ₂ evolution	Higher than plate-like BiVO ₄	2016	[196]
BiOI(001)/(110)	MO degradation	71.4% MO degradation efficiency	2018	[197]
anatase TiO ₂ (001)/(101)/SnS ₂	MB degradation	1.5 times better than pure TiO ₂	2017	[198]
anatase TiO ₂ (001)/(101)/ZnS	MB degradation	2 times better than pure TiO ₂	2017	[199]
BiVO ₄ (010)/(110)	RhB degradation	53.8% degradation efficiency within 180 min	2018	[200]
In ₂ O ₃ loaded BiVO ₄ (010)/(110)	RhB degradation	91% degradation efficiency within 180 min	2017	[201]
anatase TiO ₂ (001)/(101)	H ₂ production	a generation rate of 670 $\mu\text{mol h}^{-1} \text{g}^{-1}$	2016	[202]
CdS loaded TiO ₂ (001)/(101)	4-CP degradation	96.12% degradation efficiency	2018	[203]
anatase TiO ₂ (001)/(101)	CO ₂ Reduction	21 times increase	2014	[181]

vesting, CO₂ capture, and interface charge transfer.

Recently, Bie et al. prepared a N-doped graphene (NG) and CdS composite, the NG/CdS hollow spheres (HS) for photocatalytic CO₂ reduction [237]. The fabrication process and structure evolution of NG/CdS HS were displayed in Fig. 25(a)–(e). Using SiO₂ spheres as templates, CdS shell was first grown on the surface. Then, various amount of pyridine was added to grow NG after pyrolysis in a tube furnace. Finally, the SiO₂ spheres were removed after alkali etching, forming the hollow structure. The samples exhibit excellent CO₂ reduction activity, as shown in Fig. 25(f). Specifically, the sample CdG2

outperforms its counterparts, with a CO and CH₄ production rate of 2.59 and 0.33 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively, which are about four and five times higher than those of pure CdS. The NG contributes to the enhanced photocatalytic activity from two main aspects. On one hand, Schottky heterojunction is generated at the interface of NG/CdS (Fig. 25(g)), which prohibits the photogenerated electrons from drifting back to CdS, facilitating the charge separation. On the other hand, NG acts as the CO₂ adsorbent and activator that effectively promote the photocatalytic activity.

Besides forming heterojunctions with other materials, gra-

Table 7

Comparison of some recently developed graphene-based heterojunction photocatalysts.

Heterojunction	Type	Application	Performance	Year	Ref.
BiVO ₄ /G/ZnSe	Z-Scheme	Water splitting	9 times higher than ZnSe	2019	[209]
CsPbBr ₃ /GO	Schottky	CO ₂ reduction	A rate of 23.7 $\mu\text{mol/g h}$ with a selectivity over 99.3%	2017	[210]
BiFeO ₃ /rGO	Schottky	MB degradation	Complete degradation within 100 min	2018	[211]
Ag ₂ CrO ₄ /g-C ₃ N ₄ /GO	S-Scheme	CO ₂ reduction	1.5 times higher than Ag ₂ CrO ₄ /g-C ₃ N ₄	2018	[213]
TiO ₂ /rGO	Schottky	RhB degradation	A rate of 53.27% within 300 min	2017	[217]
rGO/ZnO	Schottky	RhB degradation	A rate of 99.6% within 180 min	2017	[218]
GO QD/TiO ₂	Type II	H ₂ evolution	100 $\mu\text{mol h}^{-1}$	2017	[219]
(BiO) ₂ CO ₃ /BiO _{2-x} /graphene	Z-Scheme	Removal of NO	2 times higher than (BiO) ₂ CO ₃	2019	[220]
ZnIn ₂ S ₄ /G	Schottky	H ₂ evolution	A rate of 40.85 $\mu\text{mol g}^{-1} \text{h}^{-1}$	2020	[221]
TiO ₂ /rGO-EDA	Schottky	H ₂ evolution	A rate of 224.9 $\mu\text{mol g}^{-1} \text{h}^{-1}$	2020	[222]
MoS ₂ /N-doped G	S-Scheme	Degradation of NH ₃	A degradation efficiency of 99.5% in 8 h	2020	[223]
N-TiO ₂ /N-doped G	Type II	MB degradation	A degradation efficiency of 87.9% within 180 min	2016	[224]
Cu ₂ O/G/TNA	Type II	CO ₂ conversion	Methanol yield of 45 $\mu\text{mol cm}^{-2} \text{h}^{-1}$	2016	[225]
P25/Ag ₃ PO ₄ /GO	Schottky	RhB degradation	75% degradation efficiency within 1 h	2015	[226]
TiO ₂ /rGO/WO ₃	Z-Scheme	Disinfection	97.3 ± 3.8% of <i>E. coli</i> inactivation within 80 mins	2017	[227]
ZnO/g-C ₃ N ₄ /rGO	Type II	MB degradation	99.5% degradation efficiency within 15 min	2015	[228]
ZnO/MoS ₂ /RGO	S-Scheme	H ₂ evolution	H ₂ production rate of 28.616 $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$	2017	[229]
Cd _{0.5} Zn _{0.5} S/g-C ₃ N ₄ /RGO	S-Scheme	H ₂ evolution	H ₂ production rate of 39.24 $\text{mmol g}^{-1} \text{h}^{-1}$	2018	[230]
ZnO/GQD	Type II	MB degradation	95% degradation within 70 min	2018	[231]
GQD/AgVO ₃	Type II	IBP degradation	5 times higher than AgVO ₃	2016	[232]
NaTaO ₃ /g-C ₃ N ₄ /G	Type II	MB degradation	99% removal of RhB within 70 min	2019	[233]
CdS/WS ₂ /graphene	Schottky	H ₂ evolution	H ₂ production rate of 1842 $\mu\text{mol g}^{-1} \text{h}^{-1}$	2016	[234]
TiO _{2-x} /rGO	Schottky	H ₂ production	H ₂ production rate of 16 $\text{mmol g}^{-1} \text{h}^{-1}$	2016	[235]

Fig. 24. (a) The schematic formation of CNNA/rGO composite in the molten salt medium. CNNA, rGO represents crystalline carbon nitride nanorods and reduced graphene oxide, respectively. (b) FESEM image of CNNA/rGO. (c) Photocatalytic CO₂-reduction property of bulk CN (bCN), CNNA and CNNA/rGO at various amount of rGO in water vapor-saturated wet CO₂ gas. (reproduced with permission [236], copyright 2019, Elsevier).

phene also acts as an ideal carrier of other semiconductor nanomaterials. He et al. [238] constructed a graphene-modified WO₃/TiO₂ S-scheme heterojunction composite photocatalyst via a facile one-step hydrothermal method, as shown in Fig. 26. The graphene sheet played two main roles in this novel composite. First, the rGO provided abundant adsorption and catalytically active sites as an ideal support. Second, the highly conduc-

Fig. 25. (a) Schematic illustration of NG/CdS HS preparation process. (b–e) Corresponding SEM images of materials sequentially appear from left to right in (a). (f) Photocatalytic CO₂ reduction performance of CdS, CdG1, CdG2, CdG3, and CdG5. (g) Schematic illustration of the charge carrier migration mechanism. CdGx: x donates that the dosage of pyridine during fabrication was 10x μL. (reproduced with permission [237], copyright 2019, Wiley).

tive rGO promoted electron separation and transfer from the conduction band of TiO₂ by forming a Schottky junction between TiO₂ and rGO. The positive cooperative effect of the WO₃/TiO₂ S-scheme heterojunction and the TiO₂/rGO Schottky heterojunction suppressed the recombination of relatively useful electrons and holes. As a result, the WO₃/TiO₂/rGO composite shows much enhanced photocatalytic H₂-evolution activity, which was ~3.5-fold that of pristine TiO₂.

4. Conclusion and outlook

This review highlights the fundamental mechanism, designing strategy and recent achievements of different kinds of heterojunction-based photocatalysts, including type II heterojunctions, PN heterojunctions, Schottky heterojunctions, S-scheme heterojunctions, surface heterojunctions and graphene-based heterojunctions. Through the discussion on the application of these heterojunction materials in H₂ production, CO₂ reduction and pollutants degradation, it indicates that photocatalysis belongs to an important candidate technology to address the vital environment crisis. The recent achievements demonstrate that forming heterojunctions provides a promising approach to enhance the activity of photocatalysts, and thus a bright prospect to a better world.

The practical applications of photocatalysts are presently hindered by insufficient activity, poor stability, and high cost. There are drawbacks for each type of heterojunctions. For example, the type II heterojunction exhibits good charge separation efficiency, the redox reactions however, take place on the relatively lower potentials of the instituting semiconductors. And for a type II heterojunction, the internal electric field is against the charge movement that the band alignment is favorable for. It needs a n-type semiconductor and a p-type semiconductor to form a PN heterojunctions. Stronger internal field requires higher doping, which challenges the doping technology. For Schottky heterojunctions, the instituting metals are usually active and lack stability under the harsh environment where photocatalysts are supposed to work. The fabrication of

Fig. 26. TEM (a) and HRTEM (b) images of the WO₃/TiO₂/rGO (WTG) composite. (c) Photocatalytic activities of various samples. (d) Schematic illustration of the S-scheme heterojunction-based charge transfer mechanism in WO₃/TiO₂/rGO composite (reproduced with permission [238], copyright 2020, Elsevier).

surface heterojunctions needs accurate control of the ratio of the exposed facets, which is extremely hard to achieve. The graphene-based heterojunctions benefit from the large surface area and high conductivity of graphene. However, it does not form new heterojunctions from the underlying mechanism.

Future opportunities in this field should fall in the following aspects. (1) In situ characterization technology. Although several theories have been proposed to explain the boosted separation of photogenerated electron-hole pairs across the heterojunction interfaces, a direct observation of the actual migration pathway of electron-hole pairs on real reactions is still missing. The improvement of the photocatalytic activity requires deeper understanding of the separation mechanism, which relies on the development of characterization equipment or technology, especially for in situ investigation. (2) New fabrication methods. Preparation of efficient heterojunction photocatalysts with a facile, controllable, and low-cost method remains challenging. New easier fabrication methods must be established to produce the engineered heterojunction materials with regulated composites, size, or morphology. Especially, methods of effective interface tuning with intimate contact between different semiconductor units are highly desirable. (3) New physical theories introducing to this field. Ultimately, the separation or recombination of electron-hole pairs roots in the movement of charged particles and the interaction with phonons. Up to date, the design of heterojunctions is accomplished within the classic theory framework. However, exotic behavior of electrons has been observed in novel materials, such as superconducting graphene or topological insulators. Possible introduction of these new physical theories in the heterojunction material field might lead to a thorough breakthrough.

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

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Advances in designing heterojunction photocatalytic materials

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This review systematically presents the working principles of various heterojunctions and summarize the recent innovative strategies for achieving high-performance heterojunction photocatalysts.

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异质结光催化材料的新进展

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摘要: 伴随着人类文明的快速发展, 一些危机慢慢显露出来, 例如能源危机、环境污染和全球变暖. 2019年5月11日, Mauna Loa天文台报告, 大气中的二氧化碳水平超过415 ppm, 达到人类历史上的最高记录, 欧盟随后于2019年11月宣布了气候紧急状态. 因此, 绿色能源技术已成为迫切需求, 以减少化石燃料的使用, 并减少污染物的产生.

光催化是直接利用太阳能的技术, 可以应用于水分解产氢、CO₂还原、降解有机污染物、促进有机物合成等, 是解决能源和环境问题的最有前途的技术之一. 光催化剂是光催化技术的核心. 目前, 许多半导体材料可作为光催化剂, 并已被充分地研究, 例如TiO₂、CdS、ZnO、BiVO₄和C₃N₄等. 然而, 单一的半导体材料具有一些缺点, 阻碍了它们的实际应用. 其中, 限制这些半导体材料光催化活性的一个关键问题是, 光生电子-空穴对容易快速复合而不是参与光催化反应. 例如, ZnO中激子的寿命估计仅为数百皮秒, 大多数激子来不及参与到氧化还原反应中.

为了抑制电子-空穴对的复合, 需要应用特殊的策略. 构建异质结光催化材料已成为最有前途的方法之一. 通常, 可以根据相邻材料的能带结构, 将异质结分为以下几种类型: PN型异质结, II型异质结, Schottky型异质结和S型异质结. 以上异质结大都是由两种半导体材料复合而形成的. 除此之外, 还可以根据形成异质结的特殊材料, 补充两种特殊的异质结类型, 即晶面异质结和石墨基异质结. 晶面异质结是由同一材料, 由于暴露不同的晶面而形成的. 石墨烯具有独特的能带结构、极大的比表面积及优良的导电性, 可以与其他半导体形成各种类型的异质结. 这些异质结材料能有效抑制电子-空穴对的复合, 从而提高材料整体的光催化活性, 也已成为光催化剂家族的重要分支. 本文详细介绍了以上各种类型的异质结光催化剂的最新进展, 概述了实现高性能异质结光催化剂的基本策略, 并对异质结光催化剂未来发展方向进行了一些探讨.

关键词: 光催化剂; 异质结; 可再生能源; 电荷转移; 氧化还原能力

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