Recent Progress on Visible Light Responsive Heterojunctions for Photocatalytic Applications

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Photocatalysis has attracted much attention in recent years due to its potential in solving energy and environmental issues. Even though numerous achievements have been made, the photocatalytic systems developed to date are still far from practical applications due to the low efficiency and poor durability. Efficient light absorption and charge separation are two of the key factors for the exploration of high-performance photocatalytic systems, which is generally difficult to be obtained in a single photocatalyst. The combination of various materials to form heterojunctions provides an effective way to better harvest solar energy and to facilitate charge separation and transfer, thus enhancing the photocatalytic activity and stability. This review concisely summarizes the recent development of visible light responsive heterojunctions, including the preparation and performances of semiconductor/semiconductor junctions, semiconductor/cocatalyst junctions, semiconductor/metal junctions, semiconductor/non-metal junctions, and surface heterojunctions, and their mechanism for enhanced light harvesting and charge separation/transfer.


1. Introduction

Global energy shortage and climate change have become the main challenges for humanity in the 21st century; thus developing alternative clean and renewable energy with high efficiency is of great significance [1]. Efficient utilization of renewable solar energy for producing zero carbon fuels from various approaches, including photocatalytic water splitting, generating valuable chemicals from photocatalytic carbon dioxide reduction, improving the environment from photocatalytic pollutant degradation, or even synthesizing value-added products such as hydrogen peroxide (H₂O₂) via photocatalytic processes, is promising to address the above issues [2–6]. Since the first discovery of photoelectrochemical (PEC) water splitting using titanium dioxide (TiO₂) as the photoanode [10], worldwide efforts have been made to exploit other efficient semiconductor photocatalytic processes due to the fact that TiO₂ with a large bandgap of 3.2 eV can only absorb ultraviolet (UV) light that accounts for just 4% of the solar light spectrum [11–13]. As visible light accounts for ca. 43% of the solar energy on the earth, it is important to develop visible light responsive semiconductors for efficient photocatalysis [14]. During the last four decades, a number of visible light responsive semiconductors including silicon [15], simple oxides (e.g. WO₃ [16,17], Fe₂O₃ [18–20], and Cu₂O [21,22]), complex oxides (e.g. BiVO₄ [23–25], Fe₃O₄ [26], and Bi₅O₃W [27]), nitrides (e.g. Ta₃N₅ [28–31], CuN [32–34]), sulphides (e.g. CdS [35,36], SnS [37], \( \text{SnS}_2 [38] \)) and \( \text{BiOX} (X = \text{Cl}, \text{Br}, \text{or I}) [39–42] \) have been developed. Also, doping large bandgap semiconductors with non-metal or metal elements such as nitrogen, sulphide, iodide, fluoride, carbon, cesium, or europium also shows good visible light responsive performance [43–53]. For example, nitrogen doped or nitrogen/sulphide co-doped CsTaWO₅ [54,55] exhibited excellent photocatalytic properties for hydrogen evolution. Moreover, sensitized large bandgap semiconductors with quantum dots (QDs) or plasmonic metals can also effectively improve the visible light absorption [56,57].

The mechanism and basic principles of photocatalysis have been described comprehensively in many recent review articles [14,58–63] which we will not repeat but only provide a brief introduction here. Semiconductors only absorb photons with the energy \( h\nu \) no less than the bandgap energy \( E_g \) and the electrons are then excited from the valence band (VB) to the conduction band (CB), generating holes in the VB [64]. The redox ability of the photogenerated electrons and...
holes depends on the CB and VB positions of the semiconductor, respectively. For example, only semiconductors possess a CB that is more negative than 0 V vs. normal hydrogen electrode (NHE) and a VB that is more positive than 1.23 V vs. NHE are able to split water into hydrogen and oxygen, as shown in Fig. 1(b). In this regard, very few semiconductors can be used for photocatalytic water splitting. On the other hand, the photogenerated electrons and holes are in the energetically unstable states and thus tend to recombine, which restricts the photoconversion efficiency. Therefore, in addition to developing promising visible light responsive semiconductors, strategies are still needed to achieve high efficiency for commercial possibility.

To suppress charge recombination, various strategies including doping\(^5\)\(^{46-53,66-68}\), the use of sacrificial agents\(^5\)\(^{62,70}\), nanostructured control\(^7\)\(^{71-73}\), crystal facet engineering\(^5\)\(^{65,74,75}\), and the formation of heterojunctions by combining a semiconductor with another semiconductor and/or metals based on band alignment\(^7\)\(^{76-77}\) have been developed in the past decades. Amongst the available strategies, the formation of heterojunctions has attracted great attention due to the effectiveness of separating photogenerated charges as well as the improvement of photocatalytic activity\(^5\)\(^{81}\). For example, the formation of Z-scheme junctions enables the use of n-type and p-type semiconductors for overall water splitting, while they can only achieve water oxidation or water reduction half reaction when used alone. Even though there are several review papers reporting heterojunctions in recent years\(^5\)\(^{59-61,63,78}\), due to the dynamic development of this research field, a comprehensive review focused on the rational design of visible light responsive heterojunctions is still necessary to provide readers with a better understanding of the state-of-the-art progress in this dynamic research field. This review article begins with an overview of low-cost and efficient methods for preparing heterojunctions, and then a brief summary of the current research status will be presented, along with the challenges and perspectives of visible light responsive heterojunctions for photocatalytic applications.

2. Methods for Fabricating Heterojunctions

Numerous techniques have been developed to fabricate heterojunctions. For example, some facile, low-cost and energy-efficient methods such as hydrothermal/solvothermal method, electrochemical deposition, chemical bath deposition, sol-gel process, and chemical precipitation are widely used to synthesize various nanostructured heterojunctions as well as heterogeneous photoelectrodes.

2.1. Hydrothermal/solvothermal methods

Hydrothermal/solvothermal methods are powerful techniques for synthesizing metal oxide and chalcogenide nanomaterials\(^7\)\(^{79-81}\). Due to the high pressure and high temperature provided during the hydrothermal/solvothermal treatments, many reactions that cannot occur in ambient conditions are able to take place. By tuning different conditions, nanomaterials with various morphologies and structures can be obtained. For example, CdS/TiO\(_2\) composites consisting of anatase TiO\(_2\) and cubic phase CdS were prepared by a one-pot hydrothermal reaction\(^82\). CO\(_2\) gas bubbles decomposed from urea created pores in the CdS/TiO\(_2\) composite increased the specific area. Chrysanthemum-analogous Bi\(_2\)O\(_3\)-Bi\(_2\)WO\(_6\) heterojunctions consisting of nanosheets were fabricated via a one-step hydrothermal route with cetyltrimethylammonium bromide (CTAB) as templates\(^83\). A new rutile–anatase core–shell TiO\(_2\) structure was synthesized using a hydrothermal method followed by calcination\(^84\). Recently, Bi\(_2\)O\(_3\)Cl/BiOCl plate-on-plate heterojunctions were obtained through a one-pot hydrothermal method\(^85\). It revealed that Bi\(_2\)O\(_3\)Cl nanosheets were grown on the BiOCl nanosheets via a crystallization, dissolution and recrystallization process during the hydrothermal reaction. Another similar junction of BiPO\(_4\)/BiOCl was also prepared by a facile one-step hydrothermal method\(^86\). β-Bi\(_2\)O\(_3\)/Bi\(_2\)S\(_3\) hybrids were constructed via a two-step solvothermal method\(^87\). β-Bi\(_2\)O\(_3\) was converted from BiO\(_2\)Cl\(_2\) nanoplate prepared using a methanol solvothermal method. Then, a certain amount of β-Bi\(_2\)O\(_3\) and thiourea was dispersed in butanol via ultrasonication, followed by the second step of solvothermal treatment. Bi\(_2\)S\(_3\) nanowires were formed on the surface of β-Bi\(_2\)O\(_3\) nanosheets. The content of Bi\(_2\)S\(_3\) could be adjusted by adding different amount of thiourea. In addition to simple heterojunctions that only consisted of two materials, multi-junctions such as C\(_3\)N\(_4\)/TiO\(_2\)/rGO can also be synthesized via a simple one-step solvothermal process\(^88\).
2.2. Electrodeposition process

Generally, electrodeposition is employed to fabricate heterogeneous photoelectrodes in a two-step procedure, where the functionality of deposited materials can be controlled by electrochemical reactions at an atomic level[89]. Recently, our group prepared Au@TiO_{2}/Al_{2}O_{3}/CuO photoelectrodes via electrodeposition[90]. The as-prepared Au@TiO_{2} particles were first cast on fluorine doped SnO_{2} (FTO) glass substrates by a doctor-blade method. After calcination, an Al_{2}O_{3} ultrathin layer was coated on the Au@TiO_{2} film via a spincoating technique, followed by heating at a hot place. Finally, the top CuO thin film was deposited via electrodeposition to form a unique Au@TiO_{2}/Al_{2}O_{3}/CuO junction. Polyaniline-sensitized TiO_{2} nanotube arrays (PANI/TiO_{2}-NTs) were also fabricated via a two-step electrodeposition process[91]. TiO_{2}-NTs were first obtained by electrochemically anodizing Ti foils, followed by depositing PANI upon the TiO_{2}-NTs through a cyclic voltammetry method. Sandwiched ZnO@Au@CuO nanorod films were synthesized similarly[92]. ZnO nanorods were electrodeposited on a stainless steel mesh substrate. Then, Au nanoparticles (NPs) were sputtered on ZnO nanorods. After calcination, CuO NPs were electrodeposited on ZnO@Au substrates to form sandwiched ZnO@Au@CuO structures.

2.3. Chemical bath deposition

Chemical bath deposition (CBD), also known as solution growth, controlled precipitation, or simply chemical deposition, is an effective method for synthesizing nanomaterials, especially metal chalcogenide quantum dots or thin films[93]. No sophisticated instruments such as vacuum system or other expensive equipment and facilities are required. Unlike electrodeposition that requires electrical conductive substrates, any substrates that are inert to the solution can be used for CBD deposition. By tuning the parameters such as bath temperature, stirring rate, pH, and solution concentration, pinhole free and uniform films are easily obtained due to the ion-by-ion growth mechanism. For instance, CdS sensitized TiO_{2} films with oriented (001) facets were prepared via a CBD method[94]. The loading of CdS NPs could be controlled by adjusting the deposition cycles. For Ag@CuO core-shell heteronanowires, the as-prepared Ag nanowires were added into the Cu precursor solution with urea; CuO shells could be coated on the Ag nanowire surfaces after the reaction[95]. A FeOOH/TiO_{2}/ZnO nanostructured junction was fabricated through a three-step CBD process[96]. ZnO nanowire arrays were first grown on FTO substrates, followed by depositing TiO_{2} shells. Finally, FeOOH nanosheets were coated on the ZnO@TiO_{2} core-shell nanowire arrays to form a three-dimensional (3D) interconnected hierarchical structure. Other heterojunctions such as AgBr/BiOBr[97], CuO/TiO_{2}[98], and CdS/TiO_{2} nanotube arrays[99] could also be obtained via CBD method.

2.4. Sol-gel process

Generally, the first step for sol-gel process is to make a sol that disperses the precursor of the target material in a polymeric liquid, followed by gelation[100]. The contained polymer can be removed by calcination. Sol-gel process has been widely used in the fabrication of heterojunctions due to its intrinsic advantages of low cost and simplicity[101–103]. For example, NiO/ZnO heterojunctions were fabricated via a sol-gel spincoating method[104]. The thickness of the ZnO layer can be tuned by simply repeating the sol-gel spincoating process. In addition to heterojunction films, sol-gel process can also be used to synthesize heterojunction powders. For instance, N-doped TiO_{2}/SrTiO_{3} heterojunctions could be synthesized by mixing the precursor solutions of TiO_{2}, SrTiO_{3}, and NH_{4}OH to form a gel, followed by calcination at 350 °C for 2 h[105]. The ratio of TiO_{2}/SrTiO_{3} in the heterojunction could be controlled by adjusting the precursor solutions.

2.5. Chemical precipitation

Chemical precipitation is a method that chemical reactions take place in liquid solutions to form solid materials, which is also commonly used for fabricating heterojunctions. For example, nanostructured CuO/TiO_{2} junction was synthesized via an alcoholic- aqueous based chemical precipitation process[106]. The weight percentage of CuO could be easily tuned by changing the concentration of the precursor solutions. BiOBr/BiOCl junction was prepared by adding KI/KBr mixed solution into the Bi(NO_{3})_{3}·5H_{2}O solution, in which the ratio of BiOBr/BiOCl could be controlled by adjusting the ratio of KI/KBr[107]. Similarly, other heterojunctions such as Bi_{2}O_{3}/ TiO_{2}, ZnMn_{2}O_{4}/TiO_{2}, and BiOBr/ZnFe_{2}O_{4} can also be prepared via chemical precipitation process[108,109].

In addition, other strategies have also been explored for the fabrication of heterojunctions, such as chemical vapour deposition (CVD)[110–111] atomic layer deposition (ALD)[114–118], and physical mixing method[119–121]. Multiple WS_{2}/SnS layered semiconductor heterojunctions were grown on Si wafers via ALD process[122]. WS_{2} films were initially deposited on Si wafers via ALD with WCl_{6} and H_{2}S (9%, balance Ar) as precursors. Then, SnS top layers were grown from tin (II) acetylacetonate and H_{2}S. Controlling the temperature over 300 °C was important to obtain pure phase SnS films. Even though CVD and ALD are powerful techniques to prepare high quality heterojunctions, the requirements of high vacuum and intensive energy input inevitably increase the cost, thus hindering their practical applications. Therefore, the modification of the current wet chemical methods and the development of other low-cost and effective methods are still needed for the advancement of heterojunctions.

3. Classification of Visible Light Responsive Heterojunctions

Visible light responsive photocatalysts are fundamentally important for efficient photocatalysis. The design and synthesis of visible light responsive heterojunctions have been focused on the improvement of light harvesting, suppression of photogenerated charge recombination and enhancement of photocatalytic activity[61–78]. According to the materials involved, heterojunctions can be primarily divided into five types: semiconductor/semiconductor (S/S) junctions, semiconductor/cocatalyst (S/C) junctions, semiconductor/metal (S/M) junctions, semiconductor/non-metal (S/N) junctions, and surface heterojunctions.

3.1. S/S junctions

Based on the band arrangements of semiconductors, S/S junctions can be classified into straddling gap (type I) junctions, staggered gap (type II) junctions, and broken gap (type III) junctions[79]. Amongst these three junctions, type II junctions are the most effective structure for the separation of photogenerated electrons and holes, which has been widely studied in recent years[123]. According to the mechanism of charge transfer and separation between the contacted semiconductors, three efficient junctions including p–n junctions, n–n junctions and Z-scheme
3.1.1. p–n Junctions

The fabrication of p–n junctions composed of p-type and n-type semiconductors is effective to separate the photogenerated electrons and holes due to the formation of built-in electrical potential in the interfaces caused by the equilibration of Fermi levels, which transfers the photogenerated electrons from the CB of the p-type semiconductor to that of the n-type semiconductor while driving the holes from the VB of the n-type semiconductor travelling to that of the p-type semiconductor (Fig. 2).

Combining narrow bandgap p-type semiconductors with large bandgap n-type semiconductors such as TiO$_2$ and ZnO to form p–n junctions not only shifts the light absorption edge from UV region to visible light region, but also effectively reduces the recombination of photogenerated holes and electrons. In recent years, visible light responsive p–n junctions such as Ag$_2$O/TiO$_2$[124], Cu$_2$O/TiO$_2$[125], Cu$_2$O/TiO$_2$[126], BiO/TiO$_2$[127], CuBr$_2$O$_2$/TiO$_2$[128], CuO/TiO$_2$[129], CuIn$_2$O$_3$/TiO$_2$[130], CuIn$_2$O$_3$/TiO$_2$[131], Cu$_2$ZnSnS$_4$/TiO$_2$[132], graphene oxide (GO)/TiO$_2$[133], Co$_3$O$_4$/TiO$_2$[134], ZnFe$_2$O$_4$/TiO$_2$[135], CdTe/TiO$_2$[136], CuInSe$_2$/TiO$_2$[137], Cu$_2$O/ZnO[138], CaFe$_2$O$_4$/ZnO[139], Cu$_2$O/ZnO[140], CuIn$_2$ZnO$_4$[141], CuInSe$_2$/ZnO[142], and BiO/ZnO[143] have been prepared for photocatalytic water splitting, photocatalytic CO$_2$ reduction and photocatalytic pollutant degradation. For example, Cu$_3$N nanocubes obtained by a thermal decomposition method were used as reactive templates to form CuO/TiO$_2$@Cu$_3$N hollow nanocubes for photocatalytic conversion of CO$_2$ into methane (Fig. 3)[129]. Such p–n junctions could absorb solar energy up to 600 nm, exhibiting a good conversion rate of 41.3 ppm g$^{-1}$ h$^{-1}$, which was 2.5 times faster than that of Degussa P25 TiO$_2$ (Fig. 3(e)). Similar enhancement of light absorption edge and photocatalytic methyl orange degradation was also observed in GO/TiO$_2$ p–n junctions when compared to P25[133]. With a bandgap of 1.2 eV, p-type Ag$_2$O was applied to sensitize a large bandgap semiconductor of n-type NaTaO$_3$, which exhibited higher photocatalytic activity for RhB degradation under visible light illumination ($\lambda$ > 425 nm) when compared to pure Ag$_2$O and NaTaO$_3$ alone[144]. Visible-light-excited electrons could easily transfer from the CB of Ag$_2$O to that of NaTaO$_3$, achieving effective charge separation. On the other hand, sensitizing large bandgap p-type semiconductor of NiO with a narrow bandgap n-type semiconductor such as CdS to form NiO/CdS p–n junctions showed enhanced photocatalytic activity for hydrogen evolution with an apparent quantum yield (AQY) of 65%[145].

To further increase light harvesting, it is more desirable to exploit p–n junctions in which both p-type and n-type semiconductors are able to be excited by visible light. For instance, NIS modified CdS nanorod p–n junction exhibited an impressive H$_2$-generation rate of 1131 μmol h$^{-1}$ g$^{-1}$ under visible light illumination, which was much higher than that of the optimal Pt/CdS[146]. The enhancement of photocatalytic activity was mainly due to the formation of p–n junctions that effectively reduced the recombination of photoexcited electrons and holes. MoS$_2$/CdS p–n junction fabricated by a facile two-step route via electrodeposition followed by chemical bath deposition exhibited a super high photocurrent density of 28 mA cm$^{-2}$ and an incident photon to electron conversion efficiency (IPCE) of ~28% at 420 nm at 0 V vs. Ag/AgCl[147]. The p-type MoS$_2$ in this junction not only enlarged the absorption of visible light region, but also prevented photocorrosion of CdS due to the formation of p–n junctions that effectively separated electrons to CdS and holes to MoS$_2$. Similarly, p-type MoS$_2$ nanoplatelets were deposited on n-type nitrogen-
doped reduced graphene oxide (n-rGO) nanosheets to form MoS$_2$/n-rGO p–n junctions exhibiting significant photocatalytic activity for H$_2$ generation in a wide spectral range between UV light and near-infrared (IR) light.[148] Some other high performance p–n junctions including BiOCl/BiVO$_4$[149], BiOI/BiVO$_4$[150], CuO/BiVO$_4$[151], Cu$_2$O/BiVO$_4$[152], Cr$_2$O$_3$/WO$_3$[153], Fe$_2$O$_3$/WO$_3$[154], Fe$_2$O$_3$/MgFe$_2$O$_4$[155], Fe$_2$O$_3$/PbBi$_2$Nb$_3$WO$_8$[156], Fe$_2$O$_3$/TaON[157], Co$_3$O$_4$/Ti$_3$O$_7$[158], Cu$_2$O/Fe$_2$O$_3$/Fe$_2$O$_3$[159], BiOI/Bi$_3$Ti$_2$O$_7$[160], Co$_3$N$_2$/CuS[161], BiOBr/ZnFe$_2$O$_4$[162], BiOI/Bi$_2$O$_3$[163], Co$_3$O$_4$/Ta$_2$O$_5$[164], Cu$_2$O/Fe$_2$O$_3$/Fe$_2$O$_3$[165], and BiOBr/ZnFe$_2$O$_4$[166] have also been developed.

In addition, introducing other n-type semiconductors, cocatalysts, metals or even insulators into the p–n junctions are effective strategies to further improve the photocatalytic activity and durability. For example, CdTe@CdS nanocrystals sandwiched between single-layered exfoliated titania nanosheets (TiO$_2$/n$_+$) to form CdTe@CdS/TiO$_2$/n$_+$ junctions could dramatically improve the photocatalytic activity, which exhibited a H$_2$ production rate that was 43.4 times higher than pure CdTe@CdS p–n junctions under visible light illumination.[167] The impressive H$_2$ production capability of CdTe@CdS/TiO$_2$/n$_+$ junctions was attributed to excellent visible light absorption of CdTe@CdS nanocrystals and proper energy band alignment as well as the formation of p–n junctions that vastly enhanced charge separation. A unique Au@TiO$_2$/Al$_2$O$_3$/Cu$_2$O junction exhibited ~20 folds enhancement of photocurrent density (~4.34 mA cm$^{-2}$) at –0.2 V vs. Ag/AgCl under simulated AM 1.5 G solar illumination when compared to TiO$_2$-P$_2$5/Cu$_2$O junction (Fig. 4(A) and (B))[90]. The size of Au metal cores dramatically affected the photocurrent density of this junction. With a size of 120 nm, Au metal cores induced scattering effect and plasmonic-induced resonant energy transfer (PIRET) effect that enhanced IPCE in UV and visible light near IR region. Moreover, the interface layer of Al$_2$O$_3$ thin film played an important role in recombining electrons from the CB of TiO$_2$ and holes from the VB of Cu$_2$O, which suppressed photocorrosion and increased stability (Fig. 4(C)). Other multiple p–n junctions such as Pt/In$_2$S$_3$/CdS/Cu$_2$ZnSnS$_2$[165], Pt/TiO$_2$/CdS/CulnS$_2$[166], ZnO/ZnS/CdS/CulnS$_2$[167], and p-Si/TiO$_2$/Fe$_2$O$_3$[168] also showed enhanced photocatalytic performance.

Furthermore, p–n junctions can also be achieved by doping with different elements in the same semiconductors or tuning the fabricated conditions. For example, Pt/TiO$_2$/Ti/n/p-Si multiple junctions were prepared by n$^+$ doping on the surface of p-Si wafers, followed
by deposited Ti, TiO2 and Pt as protective layers and cocatalyst. With the link of redox couples such as Fe2+/Fe3+ and I−/I3−, this Pt/TiO2/Ti/n-p-Si junction exhibited excellent photoelectrochemical performance for H2S splitting at 0.2 V vs. RHE (Fig. 5). Similarly, by combining the anthraquinone/anthrahydroquinone (AQ/AQH2) and I−/I3− redox couples, a Pt/p+n-Si junction was able to reduce O2 to H2O2 and oxidize H2S to S with an overall efficiency of 1.1% under AM 1.5 G illumination without external bias (7). Moreover, n-p-Si junctions with protective layer also exhibited excellent PEC performances for water splitting (68–71). A p–n Cu2O junction obtained by adjusting the pH of the precursor solutions via electrodeposition showed high activity in photocatalytic reduction of methyl viologen due to the formation of interfacial electric field (72). Deposition of a thin Mg-doped Fe2O3 layer on pure Fe2O3 via ALD could form a p–n Fe2O3 junction, which exhibited a cathodic shift of onset potential up to 200 mV (114).

### 3.1.2. n–n Junctions

In n–n junctions, the positions of CB and VB of n-type semiconductor I are both more negative than that of n-type semiconductor II. Different chemical potentials between the two semiconductors cause band bending at the interface, forming a built-in field, which effectively drives the photogenerated electrons to move from the CB of semiconductor I to that of semiconductor II and holes from the VB of semiconductor II to that of semiconductor I (Fig. 6) [61, 173, 174].

Generally, narrow bandgap n-type semiconductors can help large bandgap semiconductors such as TiO2, ZnO and SnO2 to utilize visible light by forming n–n junctions. CdS/titanate nanotube (CdS/TNTs) junctions prepared via a simple one-pot hydrothermal method showed high activity for photocatalytic hydrogen production under visible light illumination for 120 h (Fig. 7(a)) [175]. By loading 2.0 wt% of Pt, the CdS/TNTs junctions with only 6 wt% of CdS exhibited a hydrogen generation rate of 353.4 mmol h−1, with an AQY of 25.5% at 420 nm (Fig. 7(b)). The unique structure of CdS NPs enwrapped by TNTs and the formation of heterojunctions facilitated the transfer of photogenerated electrons from the CB of CdS to that of TiO2 while leaving holes in the VB of CdS to be consumed by sacrificial reagents, which prevented charge recombination, resulting in high photocatalytic activity and good stability. Adding noble metals such as Au into CdS/TiO2 to form a sandwich-structured CdS/Au/TiO2 junction showed enhanced PEC performance, which exhibited a photocurrent density of 4.07 mA cm−2 at 0 V vs. Ag/AgCl under AM 1.5 G illumination, corresponding to a solar-to-chemical energy conversion efficiency of 2.8% (Fig. 7(c, d)) [176]. Au NPs in this system...
caused electron relay effect and plasmonic effect that increased charge separation and light absorption (Fig. 7(e)). Exfoliated TiO$_2$ nanosheets in CdS/TiO$_2$ junctions were found to suppress photocorrosion of CdS NPs and improve photocatalytic activity for oxidizing Rhodamine B (RhB) under visible light illumination.[177]

The contacted crystal facets between semiconductors in an n–n junction also influence the photocatalytic activity. For example, hexagonal ZnO disks with dominant Zn-terminated (0001) and O-terminated (0001) facets were coated with 5 wt% CdS by CVD to form ZnO disk/CdS junctions, which exhibited a hydrogen evolution rate approximately triple that of ZnO rod/CdS junctions with nonpolar (0110) facets[178]. Recently, a CdS/SnO$_2$ junction composed of screw-like SnO$_2$ nanostructure and CdS QDs was synthesized, which exhibited an impressive photocurrent density of 9.9 mA cm$^{-2}$ at 0V vs. saturated calomel electrode (SCE), corresponding to a hydrogen generation rate of 159.6 μmol h$^{-1}$ cm$^{-2}$[179]. In addition, other narrow bandgap/large bandgap visible light responsive n–n junctions such as WO$_3$/TiO$_2$[180,181], Fe$_2$O$_3$/TiO$_2$[182,183], Fe$_3$Ti$_2$O$_7$/TiO$_2$[184,185], CeO$_2$/TiO$_2$[186], AgBr/TiO$_2$[187,188], BiVO$_4$/TiO$_2$[189], CeO$_2$/SnO$_2$[190], Fe$_2$O$_3$/ZnO[191], and BiVO$_4$/ZnO[192,193] also showed enhanced photocatalytic activity under visible light illumination.

The formation of n–n junctions promotes the separation of photogenerated electrons and holes in narrow bandgap semiconductors, thus dramatically improving the photocatalytic activity when compared to the bare narrow bandgap semiconductor itself. For example, BiVO$_4$/WO$_3$ heterojunction electrodes consisting of four layers of WO$_3$ and a layer of BiVO$_4$ prepared via layer-by-layer process exhibited enhanced photoactivity by 74% compared to bare WO$_3$ and 730% compared to bare BiVO$_4$.[194] Moreover, the nanostructures of the semiconductors in n–n junctions are important for achieving high photocatalytic performance. Nanorod WO$_3$/BiVO$_4$ junctions were found to offer enhanced IPCE from 9.3% to 31% at 420 nm when compared to planar WO$_3$/BiVO$_4$ heterojunction films.[195] The enhanced PEC properties were attributed to high surface area and good charge separation at the WO$_3$/BiVO$_4$ interfaces. With Co-Pi as oxygen evolution cocatalyst, nanorod WO$_3$/BiVO$_4$ junctions exhibited a remarkably stable photocurrent density of 3.2 mA cm$^{-2}$ at 1.23 V vs. RHE under one sun irradiation.[196] Without the use of cocatalyst, WO$_3$/W-doped BiVO$_4$ core/shell nanowires (WO$_3$/W:BiVO$_4$ NWS) produced a high photocurrent density of 3.1 mA cm$^{-2}$ and an IPCE of ~60% at 300–450 nm at 1.23 V vs. RHE under AM 1.5 G illumination.[197] The optimal thicknesses of BiVO$_4$ and WO$_3$ that were
shorter than the electron and hole diffusion lengths, and electric fields formed by gradient W doping and the n–n junctions effectively prevented the recombination of photogenerated electrons and holes, resulting in high PEC performances. The photocatalytic activity of WO$_3$/BiVO$_4$ junction can be further improved by nanostructured control, doping and the use of oxygen evolution co-catalyst. For example, a WO$_3$/BiVO$_4$/FeOOH/CoPi core-shell nanostructured photoanodes composed of helical WO$_3$ arrays, W, Mo codoped BiVO$_4$ junctions and double cocatalyst layers of FeOOH/CoPi exhibited an impressive photocurrent density of ~5.35 mA cm$^{-2}$ at 1.23 V vs. RHE$^{[198]}$. Recently, WO$_3$/BiVO$_4$/CoPi core-shell nanostructured photoanodes exhibited a record photocurrent density of 6.72 mA cm$^{-2}$ under one sun illumination at 1.23 V vs. RHE$^{[199]}$, corresponding to ~90% of the theoretical value of BiVO$_4$(Fig. 8)$^{[199]}$. In addition to water splitting, WO$_3$/BiVO$_4$ junctions are also promising candidates for photocatalytic CO$_2$ reduction. Cobalt carbonate (Co-Ci) used as cocatalyst for WO$_3$/BiVO$_4$ to form WO$_3$/BiVO$_4$/Co-Ci junctions performed excellent PEC reduction for CO$_2$ in CO$_2$-saturated KHCO$_3$ (KCl, pH = 7) electrolyte, reaching an exceptional photocurrent density of 3.5 mA cm$^{-2}$ at 1.23 V vs. RHE under one sun illumination, which produced 11 times larger amount of CH$_4$ than WO$_3$/BiVO$_4$/Co-Pi junctions$^{[200]}$. In addition, other narrow bandgap n–n junctions including CdS/C$_3$N$_4$$^{[201]}$, WO$_3$/CdS$^{[111]}$, WO$_3$/C$_3$N$_4$$^{[202,203]}$, Co-doped Fe$_2$O$_3$/MgFe$_2$O$_4$$^{[204]}$, CdS/Fe$_2$O$_3$$^{[205]}$, Ti-doped Fe$_2$O$_3$/ZnFe$_2$O$_4$$^{[206]}$, Fe$_2$O$_3$/Fe$_2$TiO$_5$$^{[207-209]}$, CeO$_2$/C$_3$N$_4$$^{[210]}$, MoS$_2$/C$_3$N$_4$$^{[211]}$, CdS/Bi$_2$MoO$_6$$^{[212]}$, and WO$_3$/Fe$_2$O$_3$$^{[213]}$ have been explored. Multiple n–n junctions are proposed to further improve photocatalytic performance due to the enlargement of light absorption and better charge separation. For example, TiO$_2$/CdS/CdSe junctions exhibited remarkable enhancement of photocatalytic activity$^{[214]}$. When CdS and CdSe contacted, the Fermi level alignment occurred, forming a stepwise band edge structure in the TiO$_2$/CdS/CdSe junction, which exhibited a saturated photocurrent density of 14.9 mA cm$^{-2}$ under AM 1.5 G visible light illumination. Similarly, double-sided CdS and CdSe QDs co-sensitized ZnO nanowire arrays exhibited a significant photocurrent density of ~12 mA cm$^{-2}$ at 0.4 V vs. Ag/AgCl under visible light illumination$^{[215]}$. A TiO$_2$/ZnO/CdS/CdSe junction was reported to achieve a photocurrent density of 11.8 mA cm$^{-2}$, corresponding to photo-conversion efficiency of 6.4%$^{[216]}$. Recently, a TiO$_2$/BiVO$_4$ junction co-sensitized with C$_3$N$_4$ and graphene quantum dots (GQDs) was fabricated$^{[217]}$. This TiO$_2$/BiVO$_4$/C$_3$N$_4$/GQD junction not only avoided the use of environmental risk of metal chalcogenides, but also increased hole mobility, resulting in enhanced photocatalytic activity. ZnFe$_2$O$_4$/CdS/ZnO junctions showed enhanced photocatalytic activ-

Fig. 8. (a) Schematic illustration of the fabrication of a core-shell WO$_3$-NRs/BiVO$_4$+CoPi photoanode and the corresponding charge transfer and separation in a PEC system under light illumination. (b) Cross-sectional SEM image of the ITO/Pt/ITO/WO$_3$-NRs/BiVO$_4$+CoPi photoanode. (c) IPCE of the photoanode at different temperatures at 1 V vs. RHE. (d) I-V curves under chopped light illumination. Reproduced from Ref. [199] with permission of The CC-BY licence.

ity and stability when compared to CdS/ZnO junction alone, which was attributed to typical stair-like band alignment between ZnFe$_2$O$_4$, CdS and ZnO[218]. Moreover, adding another semiconductor with suitable bandgap position[219–221] or another carbon material with high conductivity[222–224] between the original n–n junctions to form multiple junctions can also improve the photocatalytic properties. Semiconductors with different crystal phases can form special n–n junctions. For example, cobalt doped zinc blende/wurtzite (ZB/WZ) mixed phase of ZnO junctions exhibited improved visible light photocatalytic activity for phenol and methylene blue (MB) degradation when compared to the monophasic undoped ZnO and doped Co:ZnO counterparts, which was attributed to the interfacial charge separation[225]. Similarly, a biphasic CdS junction consisting of ZB and WZ phases showed enhanced photocatalytic activity and durability for hydrogen evolution under visible light illumination without loading any cocatalysts[226]. Cd$_{1-x}$Zn$_x$S solid solution with nano-twin structures exhibited a superior photocatalytic hydrogen generation rate of 1.79 mmol h$^{-1}$ with an extremely high AQY of 43% under visible light illumination without noble metal cocatalysts[227]. The difference of Fermi level between the grains and the boundaries in the nano-twin structure drove migration of electrons, which generated a band-bending and “back to back” Schottky barrier, resulting in efficient charge separation and thus improving the photocatalytic activity (Fig. 9). This phenomenon was also found in a twin-induced Cd$_{0.5}$Zn$_{0.5}$S nanorod junction[228]. Without noble metal loading, twin-induced one-dimensional Cd$_{0.5}$Zn$_{0.5}$S junctions composed of alternating ZB and WZ segments along the [111] direction showed highly efficient charge separation and photocatalytic hydrogen generation with an extraordinary quantum efficiency (QE) of 62%. Band alignment between ZB and WZ segments led to the formation of numerous junctions in a specific dimension, which prevented the recombination of photogenerated electrons and holes, resulting in excellent photocatalytic activity. On the other hand, an n–n BiVO$_4$ junction achieved by gradient doping of tungsten exhibited a carrier-separation efficiency of up to 80%[229]. Forming a tandem cell with a double junction amorphous Si solar cell, the n–n BiVO$_4$ junction with CoPi as cocatalyst generated a photocurrent density of 4 mA cm$^{-2}$ under one sun illumination, corresponding to a solar-to-hydrogen (STH) efficiency of 4.9%.

### 3.1.3. Z-scheme junctions

Generally, Z-scheme junctions are composed of semiconductor I with CB more negative than the hydrogen generation potential, semiconductor II with VB more positive than the oxygen generation potential, and a liquid-state or solid-state electron mediator that can recombine holes from VB of semiconductor II and electrons from CB of semiconductor I, resulting in overall water splitting (Fig. 10)[230–231]. Unlike p–n junctions and n–n junctions men-

![Fig. 9](image-url) Schematic illustration of charge transfer and photocatalytic H$_2$ generation of the nano-twin Cd$_{0.5}$Zn$_{0.5}$S-PH crystals with the “back to back” Schottky barrier. (c) TEM image of the Pt loaded Cd$_{0.5}$Zn$_{0.5}$S-PH sample. Reproduced from Ref. [227] with permission of The Royal Society of Chemistry.

![Fig. 10](image-url) Schematic illustration of Z-scheme junction band alignments, and the correspondingly possible photoexcited electron-hole pair separation and transfer between the contacted semiconductors: (a) with liquid-state electron mediator, (b) with solid-state electron mediator, (c) without electron mediator.
tioned above, Z-scheme junctions are able to keep photogenerated electrons and holes in strongly redox states, which is promising for water splitting\cite{233,236}, CO\(_2\) reduction\cite{217-219} and pollutant degradation\cite{240-242}.

Redox couples such as IO\(_3^-\)/I\(^-\)\cite{235,236,243}, I\(^-\)/I\(^2-\)\cite{244,246}, Fe\(^3+\)/Fe\(^2+\)\cite{234,244} and NO\(_3^-\)/NO\(_2^-\)\cite{246} are widely used as liquid-state electron mediators for Z-scheme junctions, which can achieve overall water splitting. For example, a Z-scheme system consisting of PtO\(_2\)/WO\(_3\) as oxygen evolution photocatalyst, Pt/SrTiO\(_3\)/Cr/Ta as hydrogen evolution photocatalyst, in the presence of I\(^-\)/I\(^2-\) and IO\(_3^-\)/I\(^-\) redox mediators, was developed\cite{246}. PtO\(_2\)/H\(_2\)-Cs-WO\(_3\) obtained by thermal treated PtO\(_2\)/WO\(_3\) using Cs\(_2\)CO\(_3\) aqueous solution followed by H\(^-\)-exchange treatment in the Z-scheme system exhibited an enhanced performance under visible light illumination that was 3 times higher than the untreated counterpart. A four-electrode Z-scheme system composed of Pt/W/Mo/VI\(_2\)O\(_5\), Pt, ZnO/Co\(_3\)O\(_4\)Se, and CoS with the presence of IO\(^3-\)/I\(^-\) or Sn\(^2+\)/Sn\(^4+\) as an electron mediator could achieve unbiased PEC water splitting\cite{247}. In addition, other Z-scheme junctions such as Pt/SrTiO\(_3\)/Rh/(BiVO\(_4\)), Bi\(_2\)Mo\(_6\)O\(_{19}\) or WO\(_3\)/Fe\(^3+\)/Fe\(^2+\)\cite{234}, Ru/SrTiO\(_3\)/Rh/VI\(_2\)O\(_5\)/Co{(bpy)}\(_2\)/Ru/SrTiO\(_3\)/Rh/VI\(_2\)O\(_5\)/Co{(phen)}\(_2\)\cite{246}, Pt[(SrTiO\(_3\))/Cr/Ta]/WO\(_3\)/Pt[I\(^-\)/I\(^2-\)]\cite{246}, Pt/TaON/WO\(_3\)/Pt(Pt)[(I\(^-\)/I\(^2-\)]\(\times\)\(\times\)\cite{246}, (dye sensitized Pt/H\(_2\)Nb\(_2\)O\(_7\))/WO\(_3\)/Pt/IrO\(_2\)/I\(^-\)/I\(^2-\)\(\times\)\(\times\)\cite{246}, and MgTa\(_2\)O\(_6\)/TaON/(IO\(_3^-\)/I\(^-\))\(\times\)\(\times\)\cite{235} have been explored for overall water splitting.

Even though redox couples based Z-scheme junctions can achieve overall water splitting, these systems are limited to liquid phase photocatalytic reactions only, which hinders their applications in other fields such as photocatalytic pollutant degradation in solutions\cite{238}. Moreover, the redox couples all inevitably absorb light and their long-term stability in a wide range of pH is challenging. Therefore, all-solid-state Z-scheme systems attracted increasing attention in the past decade. Noble metals such as Au, Ir, Pt, and Ag can be used as solid-state electron mediators. For example, all-solid-state Z-scheme systems including CdS/Au/TiO\(_2\)/La/Rh)/Ir/CoO\(_2\)/Ta/ Nb\(_2\)O\(_7\)\cite{250}, Ru/(SrTiO\(_3\)/La/Rh)/Ir/CoO\(_2\)/Ta/Nb\(_2\)O\(_7\)\cite{251}, Ru/SrTiO\(_3\)/Rh/Ir/Ta/Nb\(_2\)/CoO\(_2\)\cite{252}, CdS/Au/ZnO\(_2\)\cite{255}, CdS/Au/TiO\(_2\)\cite{256} and CdS/Pt/WO\(_3\)\cite{257} have been developed for water splitting. Recently, a Z-scheme system of Ru/(SrTiO\(_3\)/La/Rh)/Au/VI\(_2\)O\(_5\)/Pt/RuO\(_2\), was reported for pure water splitting, which exhibited a STH efficiency of 1.1% under AM 1.5 G illumination and an AQY of over 30% at 419 nm (Fig. 11)\cite{258}. The STH and AQY obtained by this system were the highest values amongst Z-scheme water splitting systems based on particulate semiconductors without any external bias. Other Z-scheme systems such as H\(_2\)WO\(_4\)/H\(_2\)O/Ag/AgCl\(_2\)\cite{259}, Ag/PtO\(_2\)/Ag/Ag/AgCl\(_2\)\cite{260}, AgCl/Ag/Ir/TaON\(_2\)\cite{261}, AgCl/Ag/AgBr\(_2\)\cite{262}, Ag/Co\(_2\)O\(_3\)/Ag/Ag/AgBr\(_2\)\cite{263}, CdS/Au/TiO\(_2\)\cite{264}, Bi\(_2\)TeO\(_3\)/Ag/AgCl\(_2\)\cite{265}, GO/Ag/AgCl\(_2\)\cite{266}, C\(_3\)N\(_4\)/Ag/AgBr\(_2\)\cite{267}, and Ag/PtO\(_2\)/Ag/Sc\(_2\)O\(_3\)\cite{268} have been fabricated for organic pollutant degradation. In addition to noble metals, reduced graphene oxide (RGO) or other conductive metals can also be used as electron mediators. By using photoreduced graphene oxide (PRGO) as a solid electron mediator, a Z-scheme system of Ru/SrTiO\(_3\)/Rh/VI\(_2\)O\(_5\)/PRGO was developed for overall water splitting\cite{233}. The method to reduce GO was important for this Z-scheme system. PRGO obtained by photoexcited electrons from VI\(_2\)O\(_5\) possessed a high electron conductivity and a low degree of hydrophobicity, which effectively transferred photoexcited electrons from O\(_2\) photocatalyst to H\(_2\) photocatalyst. Fe\(_2\)V\(_2\)O\(_7\)/RGO/CdS exhibited high photo-conversion efficiency of CO\(_2\) to methane under visible light illumination due to high electronic mobility between the interfaces that facilitated ef-
icient charge separation. A ZnO/CdS system consisting of metal Cd cores and ZnO/CdS heterostructural shells was prepared for water splitting. After loading with 3 wt% Pt cocatalyst, this system exhibited a high hydrogen evolution rate of 1.92 mmol h⁻¹. The metal Cd core served as electron mediator for the recombination of photogenerated electrons from CB of ZnO and holes from VB of CdS. Moreover, the shortened charge-carrier transport length in the thin ZnO/CdS heterostructural shell also contributed to charge separation, resulting in enhanced photocatalytic activity for hydrogen evolution.

Without electron mediators, Z-scheme systems can also be formed by two semiconductors, where the photogenerated holes from VB of semiconductor I recombine with the electrons from CB of semiconductor II, leaving more reductive electrons in CB of semiconductor I and more oxidative holes in VB of semiconductor II, resulting in enhanced photocatalytic activities. A direct Z-scheme system of ZnO/CdS showed high photocatalytic activity for hydrogen generation under simulated solar light irradiation. After loading with 1 wt% Pt cocatalyst, the ZnO/CdS heterostructural junction exhibited a hydrogen evolution rate of 3870 mmol h⁻¹ due to prolonged lifetime of photoexcited carriers in the heterojunction. Similarly, the (001) oriented TiO₂/CdS system also involved direct Z-scheme electron transport mechanism, resulting in much higher photocurrent density under UV-visible light illumination than visible light only. A direct Z-scheme system of CdS/WO₃ was synthesized for photocatalytic CO₂ reduction to form CH₄ under visible light illumination. With 5 mol% CdS content, the optimized CdS/WO₃ junction exhibited a high CH₄ production rate of 1.02 μmol h⁻¹ g⁻¹, which was 100 times higher for WO₃ and 10 times higher for CdS under the same reaction conditions, respectively. Enhanced photocatalytic activity for CO₂ reduction and organic pollutant degradation was also observed in a direct Z-scheme junction of C₆H₆/N₂ when compared to pure C₆H₆/N₂. Supramolecular metal complex (RuBBr₂⁺) with [Ru(dmb)₂(BL)₂]⁻ as a photo-sensitizer unit and [Ru(BL)₂(CO)₂Cl₂]⁻ as a catalyst unit was contacted with TaON to form a TaON/RuBBr₂⁺ direct Z-scheme junction for photocatalytic CO₂ reduction. When loading with Ag NPs, the Ag/TaON/RuBBr₂⁺ junction mainly produced formic acid and formaldehyde as the reduction and oxidation products, respectively. Other direct Z-scheme junctions such as Ru/SrTiO₃/Rb:BIVO₄, C₆H₆/TiO₂, NaNbO₃/WO₃, and AgCrO₃/GO have also been developed.

3.2. S/C junctions

Cocatalysts are important for photocatalytic applications, as they could improve surface kinetics, lower activation energy or over potential, enhance photogenerated charge separation, suppress photocorrosion and increase stability of the semiconductors. Loading cocatalysts on the surface of the semiconductor to form S/C junctions is another effective strategy to improve efficiency. Take water splitting as an example: there are two kinds of cocatalysts, namely hydrogen evolution cocatalysts (HEC) and oxygen evolution cocatalysts (OEC) for water reduction and water oxidation processes, respectively. Based on the functions of cocatalysts, S/C junctions can be divided into S/HEC and S/OEC junctions, which will be discussed in the following sections.

3.2.1. S/HEC junctions

Noble metals such as Pd, Pt, Ir, and Rh have been recognized as excellent HEC for hydrogen production. However, the utilization of noble metals is not practicable for commercial applications due to the high cost issue. During the past decades, metal sulphides such as MoS₂, NiS, and WS₂ have been developed as cost-effective HEC.

MoS₂ was loaded on CdS as HEC to form CdS/MoS₂ junctions, which exhibited excellent photocatalytic hydrogen production using lactic acid solution as the sacrificial agent under visible light illumination. When loading 0.2 wt% of MoS₂ on CdS, the photocatalytic activity increased by up to 35 times when compared to bare CdS, which was even higher than that of 0.2 wt% Pt/CdS under the same conditions. Similarly, when loading with 1.0 wt% WS₂ as cocatalyst, hydrogen evolution of CdS/WS₂ increased by up to 28 times when compared to bare CdS under visible light illumination. H₂-production of C₆H₆ could also be improved when loading with 0.01 wt% of WS₂ as HEC under visible light illumination. Contacting CdS with MoS₂/graphene as cocatalyst to form CdS/MoS₂/graphene junction exhibited a hydrogen evolution rate of 1.8 mmol h⁻¹ in lactic acid solution under visible light illumination, corresponding to an AQE of 28.1% at 420 nm, which was much higher than the Pt/CdS counterpart. A NiS/ZnO/CdS /RGO junction with NiS and RGO as cocatalysts exhibited a high hydrogen evolution rate of 375.7 μmol h⁻¹ and an AQE of 31.1% at 420 nm. The positive synergetic effect between RGO nanosheets and NiS could greatly suppress charge recombination and provided a large number of active sites for photocatalytic reactions, resulting in enhanced activity for hydrogen production.

3.2.2. S/OEC junctions

Water oxidation reaction for oxygen evolution is kinetically slow due to the four-electron transfer process, which becomes the control step for water splitting. Therefore, exploring high performance OEC is of importance for water splitting. Generally, noble metal oxides such as RuO₂ and IrO₂ are excellent OEC for photocatalytic oxygen evolution. Similar to HEC, earth abundant OEC including iron compounds (FeOₓ, Co(OH)₂), cobalt compounds (Co-Pi, Co-Bi, CoOₓ, Co(OH)ₓ, Co₃O₄), and nickel compounds (NiOₓ, NiOOH) have been developed to replace the expensive noble metal oxides.

Co-Pi as one of the most effective OEC has been widely used to improve the photocatalytic performance of visible light responsive semiconductors including WO₃, Fe₂O₃, BiVO₄, SiO₂, and Ta₂N₂O₅. In addition, other S/C junctions such as Fe₂O₃/Co(OH)₂, Mo:BiVO₄/FeOOH, SiO₂/Co(OH)₂, Fe₂O₃/Co₃O₄, Sn:Zr:Fe₂O₃/NiOOH, BiVO₄/NiFeOOH-Bi, and NiFe layered double hydroxides (LDH) have been developed.
ide (LDH), Co(OH)₉, and Co-Pi were loaded on Ta₃N₅ as OECs to form a Ta₃N₅/NiFe-LDH/Co(OH)₉/Co-Pi junction, which obtained a photocurrent density of 6.3 mA cm⁻² at 1.23 V vs. RHE under AM 1.5 G illumination. Recently, an integrated complex 2/complex 1/Ni(OH)ₓ/Fh/TiOₓ/Ta₃N₅ junction consisting of two hole-storage layers (HSL) of [Ni(OH)ₓ/ferrihydrite (Fh)], coupled molecular catalysts of Co₄O₄(C₂Me)(CNpy)₄ (complex 1) and [Cp*Ir(L₁)Cl]Cl (L₁ = 2,2′-biimidazoline) (complex 2), a blocking layer of TiOₓ, and a semiconductor of Ta₃N₅, generated a record photocurrent density of 12.1 mA cm⁻² at 1.23 V under AM 1.5 G illumination (Fig. 13), which was nearly the theoretical performance of Ta₃N₅ (12.9 mA cm⁻²). In this system, photogenerated holes could be transferred to the molecular OEC for water oxidation via the photochargeable HSL, while the TiOₓ blocking layer prevented electrons from travelling to the HSL, resulting in efficient charge separation, which enabled the near ultimate performance.

3.3. S/M junctions

NPs of noble metals such as Au, Ag, and Pd have different optical properties from their bulk scale. For example, Au nanorods with different aspect ratios exhibit different light absorption bands, ranging from red to pink (Fig. 14(A–I)), while their bulk Au mother has a unique shiny gold colour. The difference in light absorption happens because when the particles of noble metals are smaller than the wavelength of the exciting light, energy will be confined in a small spatial region. This leads to the collective oscillation of the electrons within the boundary and surface of the NPs. This phenomenon is known as localized surface plasmon resonance (LSPR), which results in the corresponding optical properties of a particular morphology of metal NPs. Therefore, when loading noble metal NPs onto the surface of semiconductors, enhanced light harvesting can be achieved and the light absorption band can be tuned by simply controlling the size and shape of the noble metal NPs. Moreover, plasmonic NPs can generate high-energy electrons induced by LSPR. As shown in Fig. 14(J), electrons near Fermi level of the metals are excited to surface plasmon (SP) state that has higher energy than the CB of the semiconductor, which will then transfer to the contacted semiconductor for processing further reduction reaction. In particular, sharp edges and corners of the NPs can greatly enhance electromagnetic field, which is beneficial for charge separation. In addition to LSPR effect, the formation of Schottky barrier between the interfaces of metals and semiconductors can also prevent charge recombination. For example, when the work function of the metal is higher than that of the contacted n-type semiconductor, electrons will travel from the semiconductor into the metal to equilibrate the Fermi energy levels, resulting in excessive negative charges in the metal while excessive positive charges in the semiconductor create a Schottky barrier in the interfaces (Fig. 14(K)).

Owing to the LSPR effect discussed above, plasmonic noble metal NPs can be used to sensitize large bandgap semiconductors for visible light photocatalysis. For example, an Au/TiO₂ junction with Schottky contact was synthesized via a ligand exchange process followed by mild calcination, which showed superior photocatalytic activity to the counterpart obtained by deposition-precipitation process in dye decomposition and water-reduced hydrogen production under visible light illumination. Complete removal of ligands from the Au NPs made it possible to produce close Schottky contact of Au/TiO₂ after a mild annealing process, contributing to
improved photocatalytic activity. The nanostructure of the Au/TiO$_2$ junction and the Au particle size also significantly affect photocatalytic activity. For example, a non-centrosymmetric Janus Au/TiO$_2$ photocatalyst exhibited a hydrogen evolution rate of 1.5 mL min$^{-1}$, which was 1.7 times higher than the core-shell counterpart under visible light illumination$^{[325]}$. Moreover, hydrogen generation using Janus Au/TiO$_2$ photocatalysts was approximately 4–7 times higher than that of the Au$_{5nm}$/TiO$_2$ nanocomposites due to much stronger plasmonic near-fields and optical-absorption enhancements brought about by the large gold NPs (30–70 nm) in the Janus structure. On the other hand, corrosion and dissolution may occur if the noble metals were exposed to the reactants and the surrounding solutions during photocatalytic reactions$^{[326]}$. To achieve better durability, metal@semiconductor core-shell structures have been developed in recent years$^{[95,326–329]}$. Plasmonic metal (Pd or Au)@TiO$_2$ composite structure with well-controlled TiO$_2$ shell thickness was achieved via a two-step surface modification process, which exhibited superior photocatalytic activity for phenol degradation under visible light illumination$^{[357]}$. Synergistic effects between large surface area with high crystallinity and well-defined morphology with controllable optical properties from plasmonic effects contributed to the enhanced photocatalytic performance. In addition to noble metals, other metallic materials can also be contacted with semiconductors to form S/M junctions for enhancing photocatalytic activities. For example, the metallic/semiconducting TaB$_2$/Ta$_2$O$_5$ core/shell heterojunction produced by a vapour phase hydrothermal (VPH) process exhibited significant enhancement in photocatalytic hydrogen evolution under both UV–vis and visible light illumination when compared to the Ta$_2$O$_5$ counterpart$^{[330]}$. The metallic TaB$_2$ core in this junction could extend the light absorption range and promote charge separation, resulting in enhanced photocatalytic performance. Recently, a Co-Pi/Ag/Fe$_2$O$_3$ photoelectrode consisting of vertical grown Fe$_2$O$_3$ nanosheets on Fe foils. Ag NPs and Co-Pi as OEC exhibited an extremely stable photocurrent density of 4.68 mA cm$^{-2}$ at 1.23 V vs. RHE under AM 1.5 G illumination for 5 h (Fig. 15)$^{[331]}$. The enhanced PEC performance was attributed to LSPR effect of Ag NPs for improving light harvesting and facilitating charge transfer. Furthermore, OEC of Co-Pi not only increased charge separation but also stabilized the electrode surface (Fig. 15(f)).

In addition to enhanced photocatalytic activity, S/M junctions show an interesting phenomenon of switchable anodic and cathodic photocurrent under visible light illumination. For example, an intriguing sequence-driven anodic to cathodic photocurrent phenomenon on bilayer structures of 5 nm thick Au and 10 nm TiO$_2$ under visible light illumination was observed$^{[322]}$. Anodic photocurrent was generated when Au particles were deposited on the TiO$_2$ coated FTO substrate (FTO/TiO$_2$/Au) due to band bending formed at the electrode–electrolyte interfaces, while swapping the deposition sequence of Au and TiO$_2$ could produce cathodic photocurrent on the FTO/Au/TiO$_2$ electrode. It was found that photogenerated electrons could be trapped in the energy well formed between band bending and Schottky contact and then tunneled through the 1.6 nm thick space charge layer, resulting in a unique anodic to cathodic photocurrent conversion. Moreover, a TiO$_2$/Ag photoelectrode exhibited switchable photocurrents depending on the wavelength of illuminated light$^{[333]}$. Under UV light illumination ($h\nu < 400$ nm), the overall anodic photocurrent was mainly produced by the n-type TiO$_2$ semiconductor, while under the illumination of visible light ($400$ nm $< h\nu < 850$ nm), the photoactive Ag nanocrystals (~3 nm) with molecule-like discrete bands contributed to the cathodic photocurrent.

### 3.4. S/N Junctions

Non-metal materials such as carbon quantum dots (CQDs), graphene nanosheets (GNs), carbon nanotubes (CNTs) and molecular systems (MSs) are contacted with semiconductors to form S/N junctions, which can reduce recombination of photogenerated electrons and holes (electrons or holes collector, Fig. 16(a)), extend the excitation wavelength (sensitizers, Fig. 16(b)), and prevent the photocorrosion (protective layer, Fig. 16(c)), resulting in enhanced photocatalytic activity as well as durability$^{[41,55,334–340]}$. According the materials involved, S/N junctions can be divided into S/CQD junctions, S/GN junctions, S/CNT junctions and S/MS junctions.
3.4.1. S/CQD junctions

Similar to conventional semiconductor QDs, CQDs also show properties of fluorescence emissions.

Nevertheless, photoexcitation in CQD is attributed to π-plasmon absorption in the core carbon NPs, which is different from conventional semiconductor QDs attributed to the quantum confinement effect. Compared to conventional semiconductor QDs such as CdS, CQDs are promising sensitizers to increase light harvesting in photocatalysis due to the intrinsic advantages such as non-toxicity, earth-abundance, and broad light absorption range (near-IR), which has attracted great attention in recent years.

Moreover, CQDs exhibit high photocatalytic activity for decomposing hydrogen peroxide, which is also beneficial for hydrogen generation. For example, CQD/C₃N₄ junctions exhibited a quantum efficiency of 16% at 420 ± 20 nm, and overall solar energy conversion efficiency of 2.0%.

The CQD/C₃N₄ junction kept high activity for overall water splitting with robust stability in 200 runs of recycling use over 200 days under visible light illumination (Fig. 17). The high activity and excellent stability of the CQD/C₃N₄ junction for water splitting was due to the two-electron/two-electron two-step pathway mechanism where water was first split into hydrogen and hydrogen peroxide by C₃N₄, while hydrogen peroxide was further decomposed into oxygen and water by CQDs under visible light irradiation. In addition to hydrogen production, S/CQD junctions are also efficient for photocatalytic CO₂ reduction. For example, a CQD/Cu₂O heterojunction was demonstrated to be effective for converting CO₂ into methanol with a high rate of 55.7 μmol g⁻¹ h⁻¹ under visible light illumination. The outstanding light restriction properties of the heterojunction structure, and efficient charge transfer and separation between CQDs and Cu₂O contributed to the enhanced performance.

Fig. 15. Top view FESEM images of (a, b) Fe₂O₃ nanosheet arrays and (c) Co-Pi/Ag/Fe₂O₃. (d) HRTEM image of Co-Pi/Ag/Fe₂O₃. Insets in (a) and (d): cross-sectional image of the Fe₂O₃ film and the selected area electron diffraction (SAED) image of Co-Pi/Ag/Fe₂O₃, respectively. (e) I-t curve of Co-Pi/Ag/Fe₂O₃ photoanode at 1.23 V vs. RHE under AM 1.5 G illumination. (f) Schematic illustration of Co-Pi/Ag/Fe₂O₃ photoanode for efficient PEC water splitting. Reproduced from Ref. [331] with permission of John Wiley and Sons.

Fig. 16. Schematic illustration of S/N junction and the correspondingly possible photoexcited electron-hole pair separation and transfer between the contacted semiconductor and non-metals: non-metal materials as (a) electrons or holes collector, (b) sensitizers, and (c) protective layer.
3.4.2. S/GN junctions

GN is a two-dimensional material with excellent electronic conductivity, which can be used as an electron sink or bridge for electron transfer in photocatalytic systems, preventing the recombination of photogenerated electron-hole pairs\(^{[350]}\). Thus, S/GN junctions generally show higher photocatalytic activities when the content of GN is optimized to a proper ratio. For example, with Pt as HEC, the QE of the Sr\(_2\)Ta\(_2\)O\(_7-x\)N\(_x\) photocatalyst could be improved from 4.26% to 6.45% in the wavelength of 280–550 nm when 5 wt% GN scaffolds were incorporated into the system\(^{[351]}\). The enhanced photocatalytic activity for hydrogen evolution in this system was attributed to the excellent conductivity of GN, which served as an electron transfer highway for the collection of photogenerated electrons onto Pt cocatalysts. Similarly, a Pt/GN/CdS junction with 1.0 wt% of GN and 0.5 wt% of Pt exhibited a high hydrogen evolution rate of 1.12 mmol h\(^{-1}\) under visible light illumination with an AQE of 22.5% at 420 nm, which was approximately 4.87 times higher than that of pure CdS\(^{[352]}\). GN served as an electron collector and transporter in this system, efficiently lengthening the lifetime of the photogenerated charge carriers from CdS, which contributed to high photocatalytic activity for hydrogen evolution. On the other hand, S/GN junctions also show enhanced activity for CO\(_2\) reduction. For example, decorating TiO\(_2\) NPs on CNTs to form TiO\(_2\)/CNT junctions could extend the light absorption range from UV to visible light region, which showed significant improvement of photocatalytic activity for phenol degradation under visible light illumination when compared to pure TiO\(_2\) and the mechanical mixture of the two materials\(^{[355]}\). Efficient transfer of visible-light-excited electrons from CNTs to TiO\(_2\) due to good interfacial contact was believed to prevent charge recombination. Similarly, 1D-1D CdS/CNT junctions prepared via a simple self-assembly method exhibited remarkably enhanced photocatalytic activity for selectively reducing nitro organics to amino organics under visible light illumination, which was attributed to the unique 1D-1D morphology, efficient charge separation and enhanced visible light absorption intensity\(^{[356]}\).

3.4.3. S/CNT junctions

CNTs can act as sensitizers to increase light harvesting or as an electron sink (similar to GN) to collect electrons in photocatalytic systems, thereby improving the photocatalytic activities\(^{[336,354]}\). For example, decorating TiO\(_2\) NPs on CNTs to form TiO\(_2\)/CNT junctions could extend the light absorption range from UV to visible light region, which showed significant improvement of photocatalytic activity for phenol degradation under visible light illumination when compared to pure TiO\(_2\) and the mechanical mixture of the two materials\(^{[355]}\). Efficient transfer of visible-light-excited electrons from CNTs to TiO\(_2\) due to good interfacial contact was believed to prevent charge recombination. Similarly, 1D-1D CdS/CNT junctions prepared via a simple self-assembly method exhibited remarkably enhanced photocatalytic activity for selectively reducing nitro organics to amino organics under visible light illumination, which was attributed to the unique 1D-1D morphology, efficient charge separation and enhanced visible light absorption intensity\(^{[356]}\).
3.4.4. S/MS junctions

MSs can be passivation layers to prevent surface recombination, sensitizers to enlarge light absorption band, and cocatalysts for specific reactions \[59\]. Therefore, the formation of S/MS junctions is another strategy for efficient photocatalysis. For example, a four-electrode tandem dye-sensitized PEC cell consisting of SnO$_2$/porphyrin as electrode 1, TiO$_2$/phthalocyanine as electrode 3, and Pt as electrode 2 and electrode 4 was able to achieve simultaneously hydrogen production and hydroquinone (QH$_2$) oxidation under AM 1.5 G illumination without external bias (Fig. 18(a) and (b)) \[357\]. The different light absorption ranges of porphyrin and phthalocyanine effectively enhanced light harvesting from one direction illumination (Fig. 18(c)), and the high enough bias from the tandem system were key to achieve hydrogen generation. Moreover, S/MS junctions are also efficient for CO$_2$ reduction. For example, Ru complex of [Ru-dcbpy] was contacted with a p-type nitrogen doped Ta$_2$O$_5$ (N: Ta$_2$O$_5$) semiconductor to form a [Ru-dcbpy]/N:Ta$_2$O$_5$ junction, which exhibited highly selective formation of formic acid (over 75%) for CO$_2$ reduction under visible light illumination, corresponding to a QE of 1.9% at 405 nm \[338\]. The linkage between the complex and semiconductor played a pivotal role in improving the reaction rate.

3.5. Surface heterojunctions

In addition to conventional heterojunctions formed between different materials or different crystal phases of the same material, band alignment between different crystal facets of the same material can also form heterojunctions that promote charge separation, which has been defined as surface heterojunctions (Fig. 19(a) and (b)) \[339\]. The new concept of “surface heterojunction” has attracted increasing attention in recent years. However, only several materials such as TiO$_2$ \[361–363\], SrTiO$_3$ \[364\], CeO$_2$ \[365\], and BiVO$_4$ \[23, 366–369\] have been reported with surface heterojunctions. As TiO$_2$, SrTiO$_3$, and CeO$_2$ absorb only UV light, which is beyond the scope of this paper, we will not discuss this in detail. BiVO$_4$ can form surface heterojunctions between (010) and (110) crystal facets, resulting in the accumulation of photogenerated electrons on the (010) facets while photogenerated holes on the (110) facets under light illumination (Fig. 19(c)). The sample with Pt selectively deposited on the (010) facets whereas Co$_3$O$_4$ on the (110) crystal facets exhibited an O$_2$ evolution rate of 160.3 μmol h$^{-1}$ in the presence of NaIO$_3$ under visible light illumination (λ < 420 nm), increasing by over 160 folds and 16 folds when compared to the samples without cocatalysts and with Pt and Co$_3$O$_4$ randomly deposited on the surfaces, respectively. The enhanced performance was attributed not only to the photogenerated electron-hole separation between the (010) and (110) facets, but also to the synergetic effect of HEC and OEC selectively deposited on different facets. More fundamental understanding of the formation of surface heterojunctions may provide useful information for the design of efficient photocatalytic systems.

Fig. 18. (a) Schematic illustration of tandem dye-sensitized PEC cell for hydrogen production from QH$_2$ without external bias. (b) Hydrogen production vs. time. (c) Light absorption spectra of SnO$_2$/porphyrin (red) and TiO$_2$/phthalocyanine (green). Reproduced from Ref. \[357\] with permission of The Royal Society of Chemistry.
4. Advantages and Disadvantages of the Heterojunctions

Based on the discussion above, we would like to briefly summarize the advantages and disadvantages of the heterojunctions for photocatalytic applications mentioned in this review article, as shown in Table 1.

5. Summary and Outlook

Photocatalysis has the potential for efficient water splitting, CO₂ reduction and pollutant degradation, which is highly promising for our sustainable development. Since it is difficult to achieve high efficiency and long-term stability for single component photocatalysts due to serious charge recombination and photochemical corrosion, extensive efforts have been devoted to developing robust and efficient heterojunction systems by combining the advantages of different components. In the past few years, numerous heterojunctions including semiconductor/semiconductor junctions, semiconductor/cocatalyst junctions, semiconductor/metal junctions, semiconductor/non-metal junctions, and surface heterojunctions have been explored for improving efficiency and stability. Since utilizing visible light is the prerequisite for the development of efficient photocatalytic systems, this review provided a state-of-the-art summary on the recent progresses of visible light responsive heterojunctions for photocatalytic applications.

Although remarkable achievements have been explored, the efficiency and stability of existing heterojunction systems are still far from satisfying the requirements of commercial applications. Various factors such as the morphology, crystal structure, crystal facet orientation, dopant, interface contact and ratio of the semiconductors in a heterojunction influence the light harvesting, charge generation and separation, and surface kinetics of the redox reactions, exhibiting different photocatalytic activity and durability in the whole system. Generally, combining the advantage of one semiconductor with another one can overcome the limitations of the single component photocatalyst to some extent. However, this strategy will inevitably generate other drawbacks. For example, the formation of p–n or n–n junctions is efficient for charge separation, but the redox ability of transferred electrons and holes is weakened due to the sacrifice of potential energy. It is still challenging to keep the balance of various factors involved to achieve optimal performance. Moreover, a simple two-component heterojunction is less likely to achieve efficient light absorption, charge generation, separation and utilization. Combining different advantages of various components such as semiconductors, cocatalysts, metals and non-metals together to form multiple junctions may have more opportunities. Thus, multiple junctions may be the promising photocatalytic systems that are worth further developing. However, the research on heterojunctions, especially the multiple junction systems is only in its infancy stage, and a deeper understanding of the charge generation and transfer in the interfaces of a multiple component heterojunction is still critically important. Even though a large number of n-type semiconductors for photocatalytic oxidation reactions have been synthesized, efficient visible light responsive semiconductors are still limited. Furthermore, there is a dearth of choices of p-type semiconductors for photocatalytic reduction re-
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References

Lianzhou Wang is currently Professor and Australian Research Council (ARC) Future Fellow at School of Chemical Engineering and Director of Nanomaterials Centre, the University of Queensland. He received his PhD degree from Shanghai Institute of Ceramics, Chinese Academy of Sciences in 1999. Before joining UQ in 2004, he has worked at two leading national research institutions (National Institute of Materials Science and National Institute of Advanced Industrial Science and Technology) of Japan as a research fellow for five years. Since joining UQ, he has worked as ARC QEII Fellow (2006), Senior Lecturer (2007), Associate Professor (2010), and is now Professor (2012-) and ARC Future Fellow at School of Chemical Engineering. He is also the affiliated group leader of Australian Institute for Bioengineering and Nanotechnology. Wang’s research interests include the design and development of functional nanomaterials for renewable energy conversion and storage applications including photocatalysis, low cost solar cells and electrochemical energy storage devices. In particular, Wang has made seminal scientific contributions to the understanding of layered semiconductor metal oxide compounds which involve the intercalation, exfoliation, self-assembly and re-stacking of a variety of layered structures. The use of semiconductor nanostructures for designing thin film electrodes, porous structures and restacked nanocomposites have demonstrated their high potentials in the applications of photoelectrochemical conversion devices including solar hydrogen generation, organic pollutant decomposition and solar-to-electricity generation devices, and rechargeable batteries. In the past ten years, as a Chief Investigator, he has succeeded in winning a large number of competitive research grants including 19 ARC grants, two CSIRO Flagship Cluster projects, one major Queensland Government fund, one Corporate Research Centre (CRC) project and a number of UQ grants, totalling the research fund of over 18 million Australian dollars. Prof. Wang has contributed more than 250 original journal publications (including top ranking journals such as Chem Rev., Chem. Soc. Rev., Angew. Chem., Adv. Mater., J. Am Chem. Soc., etc.), 12 patents and delivered more than 60 plenary/keynote/invited talk at conferences/symposia, which have attracted over 8200 citations (Scopus). He is serving as Associate Executive Editor of Journal of Nanoparticle Research and Science Bulletin, and is on the editorial board of a few other journals including Journal of Materials Science and Technology. Prof. Wang has won some prestigious Fellowships/awards including STA Fellowship of Japan, ARC Queen Elizabeth II Fellowship of Australia, UQ Research Excellence Award of 2008, Scopus Young Researcher Award of 2011 (for outstanding researchers under 40 yo, Engineering and Technology, Australian Universities), and ARC Future Fellow of 2012, and is an elected Fellow of Royal Society of Chemistry. He is also serving as a member of ARC College of Experts (2016-2018).