Perspective

The development of balanced heterojunction photocatalysts

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SUMMARY

Heterojunction photocatalysts have attracted tremendous attention because of their great potential for addressing worldwide energy and environmental issues. In the evolution of heterojunction photocatalysts from bulk to atomic scale, thin-layered heterojunction photocatalysts exhibit better photocatalytic properties but at the cost of a weak built-in electric field and insufficient stability for long-term reaction. Therefore, the development of more advanced heterojunctions is fundamentally important. A heterojunction with thickness within the space charge region has been developed and is called a balanced heterojunction, where fine-tuning the thickness of the heterojunction photocatalyst within the space charge region promotes a balance between photo-to-energy conversion efficiency and recyclability. In this perspective, the fundamentals, preparation methods, and advancements of balanced heterojunctions will be comprehensively elucidated. Based on the proposed concept of solar plants, the scalability of balanced heterojunctions is highlighted. Finally, the application scope of balanced heterojunctions is also discussed, along with challenges and new directions for practical application.

INTRODUCTION

The industrial revolution was a new starting point for the surging development of industry and society, followed by a great increase in consumption of fossil fuels. With the transformation of the energy matrix, aggravation of environmental pollution is inevitable. It is extremely urgent to develop renewable energy; solar energy is inexhaustible and widely available. Over the past few decades, various strategies for solar energy utilization have been developed with solar panels or photovoltaic cells. However, there are limitations in commercialization because of the high cost of photovoltaic energy generation.1

As one of the most promising solutions, semiconductor-based photocatalysis has the characteristics of low energy input and easy construction, potentially solving energy shortage and environmental issues. In 1972, Honda and Fujishima2 first realized the proof of concept of photoelectrochemical water splitting. The pioneering work started the journey of modern photocatalysis. Since then, researchers around the world have devoted themselves to development of efficient photocatalytic systems.3–29 In simple terms, the photocatalytic reaction on a semiconductor includes the following three steps:3,30 (1) the photocatalyst absorbs incident photons with energy greater than its band-gap energy; (2) electrons are excited from the valence band (VB) to the conduction band (CB), leaving holes behind; and (3) photogenerated excitons migrate to the semiconductor surface, driving reduction and oxidation reactions with reactants. At present, low photocatalytic efficiency remains a
challenge in the field of semiconductor photocatalysis, stemming from rapid recombination of photogenerated electron-hole pairs and irreconcilability between broad sunlight absorption and sufficient redox ability. For a one-step excitation system using a single photocatalyst, as is known to all, it is almost impossible to simultaneously satisfy the multiple performances. Hence, the concept of composite photocatalysts, which combine the merits of different materials, emerged, and this trend is necessary and inevitable. For composite photocatalytic systems, rational design of heterojunctions is one of the core strategies because of their great effectiveness in improving the photocatalytic reaction process, and tuning of heterojunction thickness is an important factor affecting the electronic properties of photocatalysts. In early research, most heterojunctions were composed of two bulk-type photocatalysts and relied on type II charge transfer (Figure 1). Despite many efforts, bulk-type heterojunction photocatalysts cannot effectively prevent rapid recombination of charge carriers and absorb sufficient light at thick thickness, and there is a lack of surface reactive sites. As preparation technology advances, two-dimensional (2D) heterojunctions are gaining more attention, and most are based on the S-scheme charge transfer mechanism (Figure 1) for spatial separation of photogenerated carriers. Compared with bulk photocatalysts, thin-layered photocatalysts possess a larger surface-to-volume ratio and enhanced response to photoexcitation, which seems to be able to address these shortcomings. However, the ultra-thin thickness hinders recycling of heterojunction photocatalysts, and the weak built-in electric field makes the conclusion debatable that thin-layered heterojunctions rely on interplanar coupling to ensure sufficient charge hopping. For this reason, it is worth considering whether the efficient light absorption and exciton transport can exist stably under long-term operation. Therefore, in the field of photocatalysis, more pioneering heterojunctions as well as suitable preparation methods are still under exploration.

Tuning the thickness of the heterojunction into the space charge region between bulk and 2D scales is a potential approach to achieve this goal because it promotes a balance between photo-to-energy conversion efficiency and durability. Taking into consideration such key features, these are called balanced heterojunctions. Figure 1 shows the origin and necessity of exploring the equilibrium region, i.e., constructing a balanced heterojunction photocatalyst, in the development of photocatalytic...
technology. Photosynthesis provided inspiration for construction of photocatalytic systems. Bulk and 2D heterojunctions that depend on a variety of heterostructures have emerged, but synergistically achieving efficiency and durability remains a challenge. In comparison, a balanced heterostructure exhibits a striking advance under suitable thickness tuning. Not only is it feasible and effective to improve the electronic properties of the heterojunction, such as preserving the redox ability of catalysts, separating electron-hole pairs, as well as absorbing more visible light, but the system is highly stable and, thus, practically usable. The significance of balanced heterojunction photocatalysts is unquestionable, and they will become an emerging area of research in the field of photocatalysis.

In view of this situation, this perspective will provide fundamental insights into the principle and preparation method of balanced heterojunction photocatalysts and conduct an in-depth discussion of the current challenges and complex changes of photocatalytic properties for these emerging heterojunctions. A reasonable design and prospects for such heterojunctions are proposed from the aspect of commercial application of solar energy. We hope that this perspective on balanced heterojunctions will provide some stimulating viewpoints and guidelines for future development of semiconductor photocatalysis.

**IMPORTANCE OF THE EQUILIBRIUM REGION AND THICKNESS REGULATION IN PHOTOCATALYSIS**

Tuning the thickness of the heterojunction to the space charge region significantly affects redox ability, absorption of visible light, transport and separation of photo-generated carriers, and recycling of the photocatalytic system. A reasonable balance between these properties enables the system to maintain long-term stability with reliable photocatalytic efficiency. Balanced heterojunctions derived from the trade-off between bulk and 2D catalysts are expected to achieve this goal and demonstrate advantages in practical applications and commercialization of heterojunction photocatalysts. Hence, the following sections will focus on the underlying mechanisms, research situations, and challenges of balanced heterojunction photocatalysts after introducing the research advancements of bulk and 2D heterojunction photocatalysts.

**Development of bulk-type and thin-layered heterojunctions**

A number of bulk-type photocatalysts of different shapes and sizes have been fabricated since the groundbreaking work in 1972. Benefitting from simple preparation and recyclability, research on bulk heterojunction photocatalysts has always been indispensable and received considerable attention. In 2015, Lv et al. prepared a g-C3N4/ZnO bulk heterojunction photocatalyst via a chemical deposition method. The photocatalytic performance toward dye degradation of g-C3N4/ZnO composites is evaluated. Altering the mass ratio of g-C3N4, the degradation rate of rhodamine B (RhB) is improved to 94% after 2 h. This phenomenon is due to the roles of the heterojunction and attached g-C3N4 in increasing the migration of photoexcitons and the contact area with the solution, respectively. One year later, Zhao et al. developed a BiVO4@MoS2 bulk-type heterojunction with a core-shell structure. Under the condition of adjusting the shell thickness, BiVO4@MoS2 samples exhibit a higher reduction of Cr6+ and oxidation of crystal violet (CV) because of the high specific surface area and strong adsorption capacity for pollutants. Effective suppression of charge recombination by the heterojunction is one of the contributive factors to enhance photocatalytic activity. Numerous efforts have been made regarding bulk photocatalysts, but they still face several challenges, including...
difficulty of exciton transport and insufficient light transmittance and reaction surface area. Finding the optimal heterostructure and tuning the thickness of the catalyst to a suitable region are crucial for enhancing the photocatalytic activity of bulk heterojunction photocatalysts.

Recent years have witnessed a spurt of progress in photocatalytic technology, and 2D heterojunction photocatalysts emerged and were first prepared by Harada et al.\textsuperscript{47} in 2002 to solve the abovementioned defects. The reduction in dimensionality optimizes charge carrier migration and light-harvesting ability. Interest in heterojunction photocatalysts continues to rise because of enhancements in photocatalytic performance that are attributable to these improvements. Khan et al.\textsuperscript{48} designed a g-C\textsubscript{3}N\textsubscript{4}/Ti\textsubscript{3}C\textsubscript{2} thin-layered heterojunction with TiO\textsubscript{2} nucleates in which the reaction rate of H\textsubscript{2} reaches 51.24 $\mu$mol g\textsuperscript{-1} h\textsuperscript{-1}, and that of CO reaches 73.31 $\mu$mol g\textsuperscript{-1} h\textsuperscript{-1}. Rutile-anatase TiO\textsubscript{2} prepared by etching with different concentrations of hydrogen fluoride is used as the mediator to transfer charges. Benefiting from the electronic coupling between the catalysts and the efficient charge-carrier separation in the thin-layered heterojunction, the photogenerated electron-hole pairs in the heterojunction photocatalyst are, respectively, accumulated on Ti\textsubscript{3}C\textsubscript{2} and g-C\textsubscript{3}N\textsubscript{4}, realizing efficient dry reforming of methane (DRM) based on a carbide/nitride-based (MXene-based) hybrid system. This enhancement is inseparable from the high adsorption capacity of g-C\textsubscript{3}N\textsubscript{4} and TiO\textsubscript{2} for CO\textsubscript{2} and CH\textsubscript{4} that further enhances the photocatalytic yield of syngas.

More recently, more efforts have been made regarding 2D heterojunction photocatalysts with S-scheme heterostructures. In this heterostructure, electrostatic attraction is considered to be the main driving force of charge transfer,\textsuperscript{49} and the path of charge transfer is similar to that of the step (Figure 1). Ultimately, photogenerated electron-hole pairs are spatially separated and accumulate on the photocatalysts with higher reduction potential and oxidation potential, respectively. For instance, Wang et al.\textsuperscript{50} showed that the coupling of aza-conjugated microporous polymers (CMPs) with C\textsubscript{2}N ultrathin nanosheets to construct the S-scheme heterostructure is one of the effective routes to achieve photocatalytic overall water splitting. Specifically, aza-CMP and C\textsubscript{2}N play, respectively, the role of O\textsubscript{2}- and H\textsubscript{2}-evolving catalysts in heterojunctions, and reduced graphene oxide (RGO) nanosheets are used as electron mediators for shuffling electrons. As a result, useless holes and electrons recombine at the interface of the aza-CMP/C\textsubscript{2}N heterojunction because of the S-scheme charge transfer mechanism and the existence of RGO while other excited carriers are retained. The solar-to-hydrogen (STH) efficiency of the optimized heterojunction photocatalyst reached 0.40% without co-catalysts, highlighting the potential of polymer photocatalysts in the field of photocatalysis. Another example is that Zhao et al.\textsuperscript{12} fabricated a thin-layered heterojunction by linking a series of boron-doped and nitrogen-deficient g-C\textsubscript{3}N\textsubscript{4} nanosheets via an electrostatic self-assembly strategy. After using Pt and Co(OH)\textsubscript{2} as co-catalysts for the evolution of H\textsubscript{2} and O\textsubscript{2}, respectively, the heterojunction photocatalyst achieved an STH efficiency of 1.16%, a hydrogen evolution rate of 62.69 $\mu$mol h\textsuperscript{-1}, and an oxygen evolution rate of 31.12 $\mu$mol h\textsuperscript{-1}, which is much higher than that of the pristine g-C\textsubscript{3}N\textsubscript{4} components. Here, the improvement of photocatalytic activity can be attributed to the enhanced spatial separation of photogenerated carriers with the help of the interfacial interaction and S-scheme charge transfer route.

The rich reactive centers, large surface-to-volume ratio, lower escape energy, as well as interlayer charge transfer resistance indicate the superiority of thin-layered heterojunctions in the field of photocatalysis. However, the weak built-in electric field
makes it difficult to ensure sufficient charge hopping, resulting in a decrease in photocatalytic efficiency. It still remains a challenge for the heterojunction photocatalyst to realize the ultimate goal in sustainable energy research: commercial utilization of solar energy. The key to realizing this goal is to design a photocatalytic system with excellent stability and recyclability that can efficiently realize photocatalytic reactions for a long time, but these important characteristics deteriorate rapidly when the heterojunction thickness reaches atomic dimensions. More advanced heterojunction photocatalysts that can balance efficiency and stability need to be developed.

**Fundamentals of balanced heterojunctions**

During the exploration and evolution from bulk-type to thin-layered heterojunctions, heterojunctions with intermediate thickness, balanced heterojunctions, were ignored because of the difficulty of preparation and insufficient research on the structure-property relationship, but they are worthy of in-depth insights. Here we start with the fundamentals of balanced heterojunctions, followed by research progress and current challenges in developing such heterojunctions.

In view of the similarity of charge-transfer modes between balanced heterojunctions and S-scheme heterojunctions, it is a feasible strategy to illustrate the photocatalytic process of balanced heterojunctions from the spatial separation mechanism of photogenerated carriers in S-scheme heterojunctions. However, S-scheme heterojunctions with bulk thickness are discussed here. Electron-hole pairs are generated when the semiconductor that can be used to construct an S-scheme heterojunction photocatalyst absorbs photons with energy greater than its band-gap energy. The Fermi level of photocatalyst A is higher than that of photocatalyst B, resulting in spontaneous diffusion of electrons and formation of the built-in electric field. Under the action of the built-in electric field and Coulombic attraction, the useless holes in the VB of photocatalyst A are inclined to recombine with the useless electrons in the CB of photocatalyst B, whereas the sufficient electrons in the CB of photocatalyst A with the higher reduction potential and the holes in the VB of photocatalyst B with the higher oxidation potential are preserved and migrate to the surface, driving the reduction and oxidation reaction with reactants on the semiconductor surface. A notable phenomenon, however, is that, when different bulk materials constructing the heterojunction photocatalyst are in contact, bending of the energy band arises at the space charge region because of the Fermi level difference, a phenomenon that may significantly impair the redox ability and material selectivity of the photocatalytic system. The problem encountered by the S-scheme heterojunction can be addressed here by tuning the thickness of the heterojunction within the space charge region on the basis that each thickness-dependent position in the band-bending region represents the corresponding redox ability (Figure 2A). As a result, photogenerated electron-hole pairs can be separated efficiently at strong redox potentials, which is the advantage of balanced heterojunctions, and it would be of great value for improving the thermodynamic and kinetic behavior of most of heterojunctions proposed so far.

It is clear that the premise of constructing a balanced heterojunction photocatalyst is to tune the thickness of the heterojunction within the space charge region, and therefore it is necessary to provide the calculation method of space charge layer thickness. $d$. $d$ can be determined by the following equations:

$$d_1 = \sqrt{\frac{2\epsilon_1 \epsilon_0 N_V V_D}{qN_r (\epsilon_1 N_1 + \epsilon_2 N_2)}}$$  \hspace{1cm} (Equation 1)
Here, $d_1$ and $d_2$ are the widths of depletion regions of different semiconductors constructing the heterojunction, $\epsilon_1$ and $\epsilon_2$ are the dielectric constants of different semiconductors, $N_1$ and $N_2$ are the impurity concentrations of different semiconductors, and $V_D$ is the built-in potential difference. For a given semiconductor material, the dielectric constant and impurity concentration are known, and $V_D$ can be obtained by measuring the difference between the work functions (WFs) of different semiconductors. On this basis, the $d$ of the balanced heterojunction can be calculated from Equations (1) and (2).

**Advancements of using balanced heterojunctions for converting solar energy**

So far, we have reviewed the evolution from bulk to 2D heterojunction photocatalysts, both of which still have much room for improvement regarding photocatalytic performance, emphasizing the importance of developing balanced heterojunctions.
To date, some balanced heterojunctions have been developed to maneuver the photocatalytic process for solar-driven application.

A prominent example of balanced heterojunctions enhancing the photocatalytic activity was demonstrated by Gao et al., where a low-temperature reflow method that can optimize structural defects was adopted to regulate the loading thickness of g-C3N4 nanosheets, and the overall thickness of ZnO/g-C3N4 composites varied within the space charge region. As the reflux time increases, a layer-by-layer interconnection structure with a unique π-π stacking state is obtained in the nanosheets, where the changes in electronic structure and heterojunction thickness resulted in an increase in the light absorption band and active centers and shortened the transport distance of excitons to accelerate water splitting. After refluxing for 12 h, the as-developed ZnO/g-C3N4 samples introducing the balanced heterostructure exhibited an optimal hydrogen evolution rate of 24.3 μmol g⁻¹ h⁻¹, which is 8 times higher than when using pure g-C3N4 material as a catalyst. A similar effect arose in the SiC@Zn0.5Cd0.5S core-shell nanostructure heterojunction as proposed by Bai et al. The adjustment of heterojunction thickness within the space charge region resulted in a 3.34-fold increase in the yield of H2. The researchers also explored the photodegradation of pollutants based on balanced heterojunctions. As an illustration, a core@shell CdS@TiO2 heterojunction photocatalyst was fabricated by a reflux method, with shell thickness varying from 13–22 nm. The existence of a core-shell structure and built-in electric field promotes the migration of excitons, and the suitable mass ratio of TiO2 increases the specific surface area; thus, the degradation rate of tetracycline hydrochloride (TCH) can reach 92% within 5 min, whereas that of pristine TiO2 without thickness tuning is less than 20%. The effects of different factors on photodegradation were also considered, and the results showed that an acidic environment, low concentration of pollutants, and appropriate concentration of inorganic anions (Cl⁻, SO₄²⁻) have positive effects on this process.

Thickness-tuning engineering has been proven to be an effective route to manipulate the performance of heterojunction photocatalysts. Regrettably, the research attributes this progress to optimization of charge carrier dynamics and structural modification induced by thickness tuning while ignoring the role played by the redox potential changes in semiconductors. Hence, the internal relationship between thickness tuning and redox ability of heterojunction photocatalysts remains unclear in the space charge region, and there is a lack of related research. In the following section, basic insights are given, and an attempt is made to discuss this phenomenon in depth.

**Change in redox ability of balanced heterojunctions with thickness tuning**

Recently, an Ag3PO4/CdS balanced heterojunction has been constructed for overall water splitting; the photocatalytic reaction process is shown in Figure 2B, followed by a discussion of balanced heterojunctions in terms of material selectivity.

Under light irradiation, the powerful photogenerated electrons and holes are retained in the CB of CdS and VB of Ag3PO4 for reduction and oxidation reactions, respectively. Most of the useless excitons are driven to the interface for recombination that benefits from the “step” charge transfer path of the balanced heterojunction. Photocorrosion of CdS and Ag3PO4 is minimized as a result, and the photogenerated electron-hole pairs are efficiently separated. However, the difference in Fermi level enables the CB of CdS bulk photocatalysts to undergo band
bending. In this case, CdS could not reduce H$_2$O to H$_2$ because of its CB being more positive than the reduction potential of H$_2$O/H$_2$. Photocatalytic overall water splitting occurred when the heterojunction thickness was controlled within the width of the space charge region. The redox ability of the photocatalyst is preserved, and the STH efficiency under visible light (STHVL efficiency) could be quickly increased to 0.75% by further reducing the thickness of the heterojunction photocatalysts, as shown in Figure 2C. The photocatalytic activity of the samples remained stable for 9 days (4 h/day) of the overall water splitting trial (Figure 2D). To the best of our knowledge, so far it is the only case that can directly split water into H$_2$ and O$_2$ using an Ag$_3$PO$_4$-CdS system. The good performance is inseparable from acquisition of the balanced heterojunction fabricated via layer-by-layer growth on the micropores of the substrate by electron beam evaporation and thickness tuning on this basis. Suitable preparation methods ensure that the balanced heterojunction retains flexible selectivity in materials; details are described under Preparation. In other words, it becomes feasible for the heterojunction photocatalyst to simultaneously obtain high photocatalytic efficiency, recyclability, and stability under reasonable adjustment of thickness with proper fabrication. These properties are necessary in the field of photocatalysis, such as water splitting, CO$_2$ reduction, organic synthesis, pollutant degradation, bacterial disinfection, and H$_2$O$_2$ production. According to different applications, the balanced heterojunction varies to meet their rigorous prerequisites, as shown in Table 1, where some typical materials are selected as examples to construct the corresponding heterojunctions; details are described under Application.

**Table 1. Varying the balanced heterojunction for different photocatalytic applications**

| Applications | Requirements | Examples* |
|--------------|--------------|-----------|
| Water splitting$^b$ | 1. The bandgap energy of photocatalyst A > 1.6 eV, and that of photocatalyst B > 1.6 eV. 2. The CB of photocatalyst A more negative than +0 eV vs normal hydrogen electrode (NHE) (pH 0), and/or the VB of photocatalyst B more positive than +1.23 eV vs NHE (pH 0). 3. WF of photocatalyst B > WF of photocatalyst A. | Ag$_3$PO$_4$/CdS$^{44}$ WO$_3$/TiO$_2$$^{45}$ MoO$_3$/CdS$^{46}$ MoS$_2$/CoAl double hydroxide$^{47}$ |
| CO$_2$ reduction$^c$ (Organic synthesis) | 1. Strong redox ability to overcome the large thermodynamic barrier, such as the Gibbs free energy difference of 698 kJ mol$^{-1}$ for the reduction of CO$_2$ to methanol and 800 kJ mol$^{-1}$ for the reduction of CO$_2$ to methane. 2. WF of photocatalyst B > WF of photocatalyst A. | ZnMn$_2$O$_4$/ZnO$^{48}$ TiO$_2$/CsPbBr$_3$$^{59}$ TiO$_2$/CdS$^{60}$ |
| Pollutant degradation | 1. The capacity to produce active species with strong oxidation ability, such as -O$_2^-$, -OH and h$^+$ radicals. 2. WF of photocatalyst B > WF of photocatalyst A. | Bi$_2$O$_3$/Bi$_2$SiO$_5$$^{61}$ SnFe$_2$O$_4$/ZnFe$_2$O$_4$$^{62}$ In$_2$O$_3$$^{63}$/Bi$_2$MoO$_6$/Bi$_2$MoO$_6$$^{63}$ Sb$_2$WO$_3$/BiOBr$^{64}$ |
| Bacteria disinfection | 1. High redox ability to generate reactive species, such as -O$_2^-$ radical (reduction potential of -0.33 V vs NHE at pH = 0) and -OH radical (oxidation potential of +2.8 V vs NHE at pH = 0). 2. WF of photocatalyst B > WF of photocatalyst A. | ZnO/WO$_3$$^{65}$ |
| H$_2$O$_2$ production | 1. The bandgap energy of photocatalyst A >1.6 eV, and that of photocatalyst B > 1.78 eV. 2. The CB of photocatalyst A more negative than +0 eV vs NHE (pH 0), and the VB of photocatalyst B more positive than +1.78 eV vs NHE (pH 0). 3. WF of photocatalyst B > WF of photocatalyst A. | TiO$_2$/In$_2$S$_3$$^{66}$ |

*The Ag$_3$PO$_4$/CdS heterojunction photocatalyst has been reported for water splitting. The other examples will potentially be prepared for the target applications because of their feasibility.

$^b$The uphill reaction kinetics of overall water splitting requires a photocatalyst to overcome Gibbs free energy (+237.2 kJ mol$^{-1}$).

$^c$Photocatalytic CO$_2$ reduction is an uphill reaction with large thermodynamic barrier and multiple reaction steps. Proton-assisted CO$_2$ photoreduction seems to be a more promising approach.
PREPARATION AND IDENTIFICATION OF BALANCED HETEROJUNCTIONS

Preparation

As mentioned, reasonable preparation of heterojunctions is a crucial prerequisite with respect to achieving the high photocatalytic efficiency needed for economical utilization of solar energy. Over the past several decades, scientists have been devoted to improving the preparation methods of heterojunctions, which is of great reference value for how to develop the proposed balanced heterojunctions. The traditional fabrication methods and experimental results of several typical heterojunction photocatalysts are summarized in Table 2.

The structures of photocatalysts prepared by traditional process are mostly 2D polymer nanosheets or nanoparticles, and there is an inevitable problem relating to post-separation of samples. In comparison, the structure of the deposited film on the substrate has the advantages of easy recycling, better stability, and large contact surface, so it is a preferred choice for practical applications. At present, physical vapor deposition and chemical vapor deposition are the most widely adopted methods for deposition of thin films in industrial production and have been introduced to the photocatalysis field. The former mainly includes electron beam evaporation coating (EBEC), resistive evaporation coating (REC), and plasma sputtering deposition (PSD), and the latter mainly includes low-pressure chemical vapor deposition (LPCVD), atmospheric pressure chemical vapor deposition (APCVD), and plasma-enhanced chemical vapor deposition (PECVD). According to the properties of the abovementioned materials (Table 2), the recommended deposition methods will be used to construct balanced heterojunctions (Table 3).

Here, the Ag3PO4/CdS sample is again taken as an example. Considering the need to precisely tune the thickness of the heterojunction, this photocatalytic system was prepared using electron beam evaporation (Figure 3A). After three stages of nucleation, growth, and film formation, the Ag3PO4/CdS thin film possesses the characteristic of tight interlayer contact, as schematically illustrated in Figure 3B.

The specific preparation process involves the following steps. The microporous ceramic substrate (ϕ20 mm and 1 mm thickness, 99% Al2O3), 8 g Ag3PO4, and 10 g CdS were put into the coater, and Ag3PO4 and CdS were, respectively, set as the first layer and second layer in the program. The coating conditions and

| Types | Preparation | The improved performances |
|-------|-------------|---------------------------|
| WO3/TiO2 | One-step hydrothermal method | H2 production = 245.8 μmol·g⁻¹·h⁻¹ |
| MoO3/CdS | Co-precipitation method | H2 production = 7.44 μmol·g⁻¹·h⁻¹ |
| MoS2/CoAl double hydroxide | Hydrothermal method | H2 production = 17.1 μmol·g⁻¹·h⁻¹ |
| ZnMn2O4/ZnO | Electrospinning technique and high temperature calcination | CO₂ reduction = 11 μmol·g⁻¹·h⁻¹ |
| TiO2/CsPbBr3 | Electrostatic self-assembly | CH4 production = 27.85 μmol·g⁻¹·h⁻¹ |
| TiO2/CdS | Hydrothermal method | MO degradation: 67% |
| Bi2O3/Bi2SiO5 | One-step solvothermal method | Tetracycline degradation: 93.2% |
| SnFe2O4/ZnFe2O4 | A controlled dehydroxylation process of indium-based precursors | RhB degradation: 97.5% |
| In2O3(OH)/In2O3 | Precipitation-deposition method | NO degradation: 52.9% |
| ZnO/WO3 | Co-precipitation method | Possessing antibacterial activity against different bacterial strains simultaneously, including S. aureus, P. Vulgaris, P. aeruginosa and K. pneumoniae |
| TiO2/In2S3 | Electrospinning technique and hydrothermal method | H2O2 production = 376 μmol·L⁻¹·h⁻¹ |
| Samples* | Substrate | Preparation methods | Applications |
|----------|-----------|---------------------|--------------|
| Ag₃PO₄/CdS⁴⁴ | Microporous ceramic or metal substrate | Ag₃PO₄ deposited on the substrate and CdS tightly deposited on Ag₃PO₄ by EBEC or REC (Figure 3B)* | Water splitting |
| Ag₃PO₄/CdS⁴⁴ | Conductive substrate | Ag₃PO₄ deposited on one side of the substrate and CdS tightly deposited on Ag₃PO₄, and then CdS deposited on the other side of the substrate and Ag₃PO₄ tightly deposited on CdS by EBEC or REC (Figure 4A)* | Water splitting |
| WO₃/TiO₂⁵⁵ | Microporous ceramic or metal substrate | WO₃ deposited on the substrate and TiO₂ tightly deposited on WO₃ by EBEC or REC | Water splitting |
| WO₃/TiO₂⁵⁵ | Conductive substrate | WO₃ deposited on one side of the substrate and TiO₂ tightly deposited on WO₃, and then TiO₂ deposited on the other side of the substrate and WO₃ tightly deposited on TiO₂ by EBEC or REC | Water splitting |
| MoO₃ₙ/CdS⁵⁶ | Microporous ceramic or metal substrate | MoO₃ₙ deposited on the substrate and CdS tightly deposited on MoO₃ₙ by EBEC or REC | Water splitting |
| MoO₃ₙ/CdS⁵⁶ | Conductive substrate | MoO₃ₙ deposited on one side of the substrate and CdS tightly deposited on MoO₃ₙ, and then CdS deposited on the other side of the substrate and MoO₃ₙ tightly deposited on CdS by EBEC or REC | Water splitting |
| MoS₂/CoAl double hydroxide⁵⁷ | Microporous ceramic or metal substrate | MoS₂ deposited on the substrate by EBEC or REC and CoAl double hydroxide tightly deposited on MoS₂ by LPCVD or PECVD | Water splitting |
| MoS₂/CoAl double hydroxide⁵⁷ | Conductive substrate | MoS₂ deposited on one side of the substrate by EBEC or REC and CoAl double hydroxide tightly deposited on MoS₂ by LPCVD or PECVD, and then CoAl double hydroxide deposited on the other side of the substrate by LPCVD or PECVD and MoS₂ tightly deposited on CoAl double hydroxide by EBEC or REC | Water splitting |
| ZnMn₂O₄/ZnO⁵⁸ | Microporous ceramic or metal substrate | ZnMn₂O₄ deposited on the substrate by LPCVD or PECVD and ZnO tightly deposited on ZnMn₂O₄ by EBEC or REC | CO₂ reduction |
| ZnMn₂O₄/ZnO⁵⁸ | Conductive substrate | ZnO deposited on one side of the substrate by EBEC or REC and ZnMn₂O₄ tightly deposited on ZnO by LPCVD or PECVD, and then ZnMn₂O₄ deposited on the other side of the substrate by LPCVD or PECVD and ZnO tightly deposited on ZnMn₂O₄ by EBEC or REC | CO₂ reduction |
| TiO₂/CsPbBr₃⁵⁹ | Microporous ceramic or metal substrate | CsPbBr₃ deposited on the substrate by LPCVD or PECVD and TiO₂ tightly deposited on CsPbBr₃ by EBEC or REC | CO₂ reduction |
| TiO₂/CsPbBr₃⁵⁹ | Conductive substrate | TiO₂ deposited on one side of the substrate by EBEC or REC and CsPbBr₃ tightly deposited on TiO₂ by LPCVD or PECVD, and then CsPbBr₃ deposited on the other side of the substrate by LPCVD or PECVD and TiO₂ tightly deposited on CsPbBr₃ by EBEC or REC | CO₂ reduction |
| TiO₂/CdS⁶⁰ | Microporous ceramic or metal substrate | CdS deposited on the substrate and TiO₂ tightly deposited on CdS by EBEC or REC | Organic synthesis |
| TiO₂/CdS⁶⁰ | Conductive substrate | CdS deposited on one side of the substrate and TiO₂ tightly deposited on CdS, and then TiO₂ deposited on the other side of the substrate and CdS tightly deposited on TiO₂ by EBEC or REC | Organic synthesis |
| Bi₂O₃/Bi₂SiO₅⁶¹ | Microporous ceramic or metal substrate | Bi₂O₃ deposited on the substrate and Bi₂SiO₅ tightly deposited on Bi₂O₃ by EBEC or REC | Pollutant degradation |
| Bi₂O₃/Bi₂SiO₅⁶¹ | Conductive substrate | Bi₂O₃ deposited on one side of the substrate and Bi₂SiO₅ tightly deposited on Bi₂O₃, and then Bi₂SiO₅ deposited on the other side of the substrate and Bi₂O₃ tightly deposited on Bi₂SiO₅ by EBEC or REC | Pollutant degradation |

(Continued on next page)
parameters of the ion source, E-Beam gun, and crystal monitor were properly set. When the coating conditions were met, the E-Beam gun was turned on to start deposition until the crystal monitor controlled the completion of 30-nm-thickness Ag3PO4 deposition on the substrate and 60 nm-thickness CdS deposition on the Ag3PO4 surface (Figure 3C). A small amount of Pt was deposited on CdS as a co-catalyst for the H2 evolution reaction.

Identification
To gain in-depth insights into the working mechanisms of balanced heterojunctions in various photocatalytic applications, advanced physicochemical analysis methods are required to characterize the structural features of the heterojunctions and the photocatalytic processes. Here, several identification methods are given:

| Samplesa | Substrate | Preparation methods | Applications |
|----------|-----------|---------------------|--------------|
| SnFe2O4/ZnFe2O4 | Microporous ceramic or metal substrate | SnFe2O4 deposited on the substrate and ZnFe2O4 tightly deposited on SnFe2O4 by LPCVD or PECVD | Pollutant degradation |
| SnFe2O4/ZnFe2O4 | Conductive substrate | SnFe2O4 deposited on one side of the substrate and ZnFe2O4 tightly deposited on SnFe2O4, and then ZnFe2O4 deposited on the other side of the substrate and SnFe2O4 tightly deposited on ZnFe2O4 by LPCVD or PECVD | Pollutant degradation |
| In2O3-0.5(OH)2/Bi2MoO6 | Microporous ceramic or metal substrate | In2O3-0.5(OH)2 deposited on the substrate and Bi2MoO6 tightly deposited on In2O3-0.5(OH)2 by LPCVD or PECVD | Pollutant degradation |
| In2O3-0.5(OH)2/Bi2MoO6 | Conductive substrate | In2O3-0.5(OH)2 deposited on one side of the substrate and Bi2MoO6 tightly deposited on In2O3-0.5(OH)2, and then Bi2MoO6 deposited on the other side of the substrate and In2O3-0.5(OH)2 tightly deposited on Bi2MoO6 by LPCVD or PECVD | Pollutant degradation |
| Sb2WO6/BiOBr | Microporous ceramic or metal substrate | Sb2WO6 deposited on the substrate and BiOBr tightly deposited on Sb2WO6 by LPCVD or PECVD | Pollutant degradation |
| Sb2WO6/BiOBr | Conductive substrate | Sb2WO6 deposited on one side of the substrate and BiOBr tightly deposited on Sb2WO6, and then BiOBr deposited on the other side of the substrate and Sb2WO6 tightly deposited on BiOBr by LPCVD or PECVD | Pollutant degradation |
| ZnO/WO3 | Microporous ceramic or metal substrate | WO3 deposited on the substrate and ZnO tightly deposited on WO3 by EBEC or REC | Bacteria disinfection |
| ZnO/WO3 | Conductive substrate | WO3 deposited on one side of the substrate and ZnO tightly deposited on WO3, and then ZnO deposited on the other side of the substrate and WO3 tightly deposited on ZnO by EBEC or REC | Bacteria disinfection |
| TiO2/In2S3 | Microporous ceramic or metal substrate | In2S3 deposited on the substrate by LPCVD or PECVD and TiO2 tightly deposited on In2S3 by EBEC or REC | H2O2 production |
| TiO2/In2S3 | Conductive substrate | TiO2 deposited on one side of the substrate by EBEC or REC and In2S3 tightly deposited on TiO2 by LPCVD or PECVD, and then In2S3 deposited on the other side of the substrate by LPCVD or PECVD and TiO2 tightly deposited on In2S3 by EBEC or REC | H2O2 production |

*The Ag3PO4/CdS sample with microporous ceramic substrate has been successfully prepared by EBEC for water splitting. The other samples are recommended to be prepared using the above preparation methods because of their feasibility.

Figure 3B illustrates the configuration schematic of Ag3PO4/CdS sample with microporous ceramic or metal substrate (A small amount of Pt is deposited on CdS as a cocatalyst for H2 evolution reaction). The other samples with microporous ceramic or metal substrates have the corresponding configurations similar to Figure 3B according to their compositions.

Figure 4A illustrates the configuration schematic of Ag3PO4/CdS sample with conductive substrate (A small amount of Pt is deposited on CdS as a cocatalyst for H2 evolution reaction). The other samples with conductive substrates have the corresponding configurations similar to Figure 4A according to their compositions.
(1) In situ and ex situ irradiated X-ray photoelectron spectroscopy (XPS) characterization. The shift of XPS peaks for oxidation photocatalysts before and after light irradiation presents an increase or decrease in electron density, which gives direct evidence of the migration path of charge carriers across the interface.

(2) Atomic force microscopy (AFM) characterization. The Kelvin probe force microscopy derived from AFM can be used to determine the WF while scanning the surface morphology. Thus, the WFs of the materials before and after contact can be easily obtained. Taking the Ag₃PO₄/CdS balanced heterojunction as an example, the WFs of the CdS film and Ag₃PO₄ film before contact were determined to be 4.7 eV and 6.1 eV, respectively, and 5.35 eV after contact by using the relationship of WF = 4.65 eV + e * contact potential difference, where e is the charge of an electron, and the WF of the gold probe was 4.65 eV in the test (by Kelvin probe SKP5050, KP Technology) (Figure 3D). This means that, when they come into contact, electrons migrate from the CdS film to the Ag₃PO₄ film through the intimate interface until their Fermi levels reach equilibrium.

(3) Electron paramagnetic resonance (EPR) characterization. ·O₂⁻ radicals and ·OH radicals can be detected using the EPR technique. The produced radicals can confirm that the prepared heterojunction photocatalyst possesses strong redox ability.
Femtosecond UV-visible (UV-vis) transient absorption (fs-TA) spectroscopy characterization. Fs-TA is a pump-probe time-resolved spectroscopy technique that is particularly suitable for studying the photodynamic parameters at an ultrafast time scale. For instance, Sun et al. used a 400-nm laser as a pump to obtain fs-TA kinetic profiles at 524 nm of BiVO$_4$/polymeric carbon nitride (PCN) heterojunction. Compared with pure PCN, the decay dynamics of the BiVO$_4$/PCN heterojunction exhibit a rising-falling-rising trend, where the first decline is due to decay of the pump, and the subsequent rise is due to injection of powerful electrons into PCN by BiVO$_4$, revealing the S-scheme transfer path of photogenerated carriers in such a heterojunction. Obviously, this technique is also suitable for exploring the charge transfer mechanism of balanced heterojunctions.

SUPERIOR SCALABILITY OF BALANCED HETEROJUNCTIONS

Integrating the advantages of different dimensional heterojunctions, the balanced heterojunction photocatalyst demonstrates satisfactory efficiency, recyclability, and material selectivity, which is one of the most promising strategies to build a next-generation heterojunction photocatalyst. At this opportunity, we might as well discuss the scalability of balanced heterojunctions from more perspectives, and hope that this is a correct understanding.

Prospect of industrialization

As mentioned above, the balanced heterojunction photocatalyst allows flexible coupling of a variety of materials, substrates, and geometries, even those with poor suitability for photocatalysis. Based on this, more effective configurations have been investigated to truly develop solar energy on a large scale. Figure 4A shows the configuration schematic of the bilateral-symmetry photocatalytic system based on the balanced heterojunction, taking the Ag$_3$PO$_4$/CdS heterojunction as an example. Ag$_3$PO$_4$ is deposited on one side of the conductive substrate, and CdS is tightly deposited on Ag$_3$PO$_4$. Meanwhile, CdS is deposited on the other side of the substrate, and Ag$_3$PO$_4$ is tightly deposited on CdS. Figure 4B illustrates the charge transfer mechanism of the bilateral symmetry photocatalytic system. When light illuminates the Ag$_3$PO$_4$-CdS stack, and CdS is located on the surface, the photogenerated electrons aggregate to the CB of CdS and drift to the surface, reducing H$_2$O to H$_2$. The holes in the VB of Ag$_3$PO$_4$ are transferred into the conductive substrate. Similar to the above, when the CdS-Ag$_3$PO$_4$ stack is exposed to light, the photogenerated holes drift to the surface of Ag$_3$PO$_4$ to oxidize H$_2$O into O$_2$, and the electrons in the CB of CdS migrate to the conductive substrate to recombine with the holes from the other stack. Hence, photocorrosion of CdS and Ag$_3$PO$_4$ is minimized, the photogenerated electron-hole pairs are separated efficiently, and the useful electrons and holes are retained in the high-energy bands. The thickness of the balanced heterojunction should be controlled within the width of the space charge region and be sufficiently thin for enhancing the redox ability. By stacking two photocatalysts on the conductive substrate in different orders, H$_2$ and O$_2$ can be generated through reduction and oxidation reactions, respectively. A small amount of Pt is deposited on CdS, which acts as a cocatalyst for H$_2$ evolution. The surface of Ag$_3$PO$_4$ for O$_2$ production and that of CdS for H$_2$ production are in contact with aqueous solution to enlarge the active surface area, and CdS and Ag$_3$PO$_4$ are fully stacked so that the built-in electric field is significantly enhanced. The role of the conductive substrate is to fully and rapidly transfer the holes and electrons produced by the Ag$_3$PO$_4$ and CdS photocatalysts in the bottom layer, where the conductive substrate is in ohmic contact with the heterojunction photocatalyst.
The concept of a “solar plant” is proposed, as shown in Figure 4C, where the water splitting reactor relies on a practically feasible photocatalytic system with a staggered array. The array design takes full account of the feasibility of industrial production and not only maximizes use of visible light but also makes full use of the recombination effect of the conductive substrate on photogenerated electrons and holes, greatly accelerating the separation of excitons. This structure enables the produced H₂ and O₂ to be collected separately, with the advantages of high efficiency, low cost, and easy construction, indicating that it could be the preferred choice for commercialization of solar energy in the future.

Application
A variety of forms of photocatalytic syntheses are now increasingly crucial for achieving a sustainable society, where water splitting provides a renewable energy source, CO₂ reduction and organic synthesis aim to address the problem in terms of global warming, pollutant degradation, bacterial disinfection and H₂O₂ production are closely related to environment issues and human health. However, several requirements, including strong redox ability, sufficient light absorption, efficient separation of steric photocarriers, and abundant availability of active sites, must still be met before these technologies can be practically employed in a sustainable manner. The proposed balanced heterojunction has been shown to potentially match these demands. As shown in Table 3, some typical materials have been recommended to construct such heterojunction photocatalysts because of their feasibility. Here, we show a number of instances of balanced heterojunctions and propose corresponding energy band structures according to different applications, hoping to expand the application scope of photocatalytic technology.

(1) Water splitting. A typical case is a WO₃/TiO₂ balanced heterojunction photocatalyst whose light-induced charge separation process is presented in Figure 5A. Although the CB potential of TiO₂ is −0.2 V (versus NHE at pH 0) before contact, the redox ability is remarkably reduced because of bending of the energy band arising at the space charge region after contact, which is unfavorable for reduction of H₂O to H₂. Tuning the heterojunction thickness within the space charge region, the decrease of photocatalytic driving force caused by the Fermi level difference can be effectively avoided, and at the same time, the transport distance of the carriers is reduced. As a result, more photogenerated electrons and holes migrate to the CB of TiO₂ and the VB of WO₃ to form a high reduction-oxidation ability for H₂ and O₂ production, respectively.

(2) CO₂ reduction. TiO₂/CsPbBr₃ is taken as an example, and the corresponding charge transfer route is proposed. As depicted in Figure 5B, the electrons from the CB of TiO₂ with weak reduction ability and the holes from the VB of CsPbBr₃ with weak oxidation ability are consumed, whereas the useful electrons and holes are retained in the high-energy band. Heterojunction thickness-tuning engineering overcomes the adverse effects caused by the Fermi level difference, and carriers with strong redox ability are able to reduce CO₂ and oxidize H₂O more easily.

(3) Organic synthesis. Recycling of CO₂ as a feedstock for organic synthesis is also one of the common applications in the field of photocatalysis; this process is illustrated by construction of a TiO₂/CdS balanced heterojunction photocatalyst (Figure 5C). When the heterojunction thickness is tuned within the space charge region, the kinetic behavior of photogenerated carriers in the photocatalytic system is improved. As a result, the photoinduced electrons
on the CB of CdS maintain a strong reducing ability, thus rapidly reducing CO₂ to CH₄ (reduction potential of -0.24 V versus NHE at pH 0).

(4) Pollutant degradation. A good example is the Bi₂O₃/Bi₂SiO₅ photocatalytic system, whose photocatalytic degradation process is shown in Figure 5D. Under the thickness-tuning strategy, the photoinduced holes on the VB of Bi₂SiO₅ obtain a higher oxidation ability to simultaneously oxidize H₂O/OH⁻ to form ·OH radicals and decompose organic (Org) pollutants, whereas the electrons in the CB of Bi₂O₃ cannot reduce O₂ to produce ·O₂⁻ radicals because of the CB of Bi₂O₃ being more positive than the reduction potential of O₂⁻/·O₂⁻. However, rich oxygen vacancies on the surface of Bi₂O₃ can activate O₂ to produce ·O₂⁻ radicals.

(5) Bacterial disinfection. The ZnO/WO₃ balanced heterojunction in Figure 5E is a good illustration that shows the photocatalytic disinfection process. The CB potential of ZnO is -0.4 V (versus NHE at pH 0) before formation of the heterojunction, whereas bending of the energy band after contact makes it difficult for O₂ to be reduced to ·O₂⁻ radicals in the photocatalytic reaction. A shrewd approach, thickness-tuning engineering, can induce a phenomenon where the photogenerated electrons on the CB of ZnO obtain the needed reduction ability to effectively reduce O₂ to generate ·O₂⁻ radicals, and the oxidation ability of WO₃ is also improved to oxidize H₂O to produce ·OH radicals.

(6) H₂O₂ production. A photocatalytic system based on a TiO₂/In₂S₃ balanced heterojunction is one of the feasible pathways for obtaining hydrogen peroxide (H₂O₂), and its working mechanism is shown in Figure 5F. Thickness
tuning effectively solves the band bending phenomenon stemming from the Fermi level difference after TiO$_2$ and In$_2$S$_3$ are in close contact and retains the reduction ability of photogenerated electrons on the CB of In$_2$S$_3$ and oxidation ability of photogenerated holes on the VB of TiO$_2$, enabling the TiO$_2$/In$_2$S$_3$ balanced heterojunction to efficiently generate H$_2$O$_2$ by reducing O$_2$ and oxidizing H$_2$O.

CONCLUSION AND OUTLOOK

For the purpose of truly benefiting mankind and the environment on a large scale, various strategies have been proposed to convert solar energy into chemical energy, where the significance of photocatalytic technology, also known as artificial photo-synthesis, is unquestionable in view of the substantial progress achieved. To date, bulk and 2D heterojunction photocatalysts are two research hotspots in the field of photocatalysis. Despite many efforts, the bulk heterojunction has obvious drawbacks where excessive thickness leads to insufficient light transmittance, slow migration of photogenerated carriers, and limited surface reactive sites. In this case, photocatalytic efficiency is maintained at an unsatisfactory level. Thin-layered heterojunctions aim to suppress the reverse reaction involving redox couples and extend the light absorption ability by reducing dimensionality. However, they possess a weak built-in electric field and suffer from poor photostability in long-term applications.
Hence, it is time to propose another mechanism, balanced heterojunctions, and related advancements have been made. We discover that the equilibrium region is essentially the space charge region of the heterojunction structure. At a suitable thickness, efficient separation of electron-hole pairs and high absorption of solar energy are collectively achieved, and the recyclability of the system is superior. Thickness-tuning engineering of the balanced heterojunction effectively avoids weakening of the redox ability of the catalysts stemming from the Fermi level difference. Thus, enhanced photocatalytic activity and durability are achieved. Not only is the principle of balanced heterojunctions developed, but photocatalytic reaction results are provided to illustrate the phenomenon. These achievements are inseparable from suitable preparation methods, which also ensure ultra-high freedom for material selection for the system. Considering the advantages of balanced heterojunctions in material selectivity, it is of great significance to construct such heterojunctions via selection of different typical materials to expand the application range of photocatalysis in industrial H₂ generation, CO₂ photoreduction, and medical science. To pursue the ultimate goal of sustainable energy research, large-scale development of solar energy, bilateral symmetry balanced heterojunction photocatalysts and a concept of a solar plant based on a staggered array design are proposed. We hope that this perspective will provide an efficient and economical prototype for construction of next-generation photocatalytic technology.

Overall, the thickness within the width of the space charge region is in an interesting region between 2D nanostructures and conventional heterojunction structures. To accelerate practical applications of artificial photosynthesis, the balanced heterojunction photocatalyst still faces numerous obvious challenges.

1. Development of advanced morphology engineering and interface regulation is necessary, such as defect engineering to maneuver the electronic band structure of heterojunctions, doping to tune the electronic properties of semiconductors, and facet engineering to optimize reactions on catalyst surfaces.
2. Balanced heterojunctions create a strong driving force for the photocatalytic reaction by retaining the redox potential of the catalyst, whereas the actual photocatalytic process and exciton migration route are debatable. Solving this issue not only depends on more powerful and suitable characterization methods but also needs focus on advanced theoretical calculation and modeling methods.
3. It is imperative to develop novel photocatalyst materials for preparation of heterojunctions, such as active materials capable of harnessing red or near-infrared light that can acquire a higher solar energy conversion efficiency at a competitive cost and photostability for long-term applications, which calls for thousands of researchers to invest in this exciting field.

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AUTHOR CONTRIBUTIONS
D.Z. and Z.D. conceived the perspective and co-wrote the manuscript. C.Z. added valuable comments to the manuscript and helped write parts of the draft. F.L. and W.H. provided supervision throughout the manuscript-writing process.
DECLARATION OF INTERESTS
The authors declare no competing interests.

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