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Internal electric field in carbon nitride-based heterojunctions for photocatalysis

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Abstract

Carbon nitride is one of the most promising metal-free photocatalysts to harvest solar light for energy conversion and pollutant treatment. Unfortunately, its photocatalytic performance is impeded by the sluggish charge carriers due to the high symmetry of unit cells of chemical structure. Fabrication of an internal electric field (IEF) in carbon nitride-based photocatalysts is evidenced to be a productive strategy to actuate the fast separation of photo-excited charge carriers and navigate their migrations to active sites for high apparent quantum efficiency (AQE) and throughputs. In the current work, a comprehensive review of IEF in different types of carbon nitride-based heterojunctions will be well presented. Emphasis will be put on the latest progress of IEF generation by hosting 2-dimensional (2D) carbon nitride nanosheets with different dimensional materials, IEF modulation by interfacial engineering as well as IEF identification and monitoring. Relationships between IEF and photocatalytic performances in various processes will also be enlightened. Finally, this review will suggest the challenges and future perspectives of IEF-driven photocatalysis. This review brings the intrinsic impetus of charge carriers in a photocatalyst to the forefront and is anticipated to provide guidance to configure powered IEF in 2D carbon nitride-based heterostructures toward efficient energy conversion and environmental purification.

1. Introduction

Excessive depletion of fossil fuels has been triggering a chain of global issues, including severe energy crisis, environmental deterioration and unpredictable climate change [1]. Therefore, it is extremely urgent to explore a green and efficient approach to make use of renewable energy for sustainability. In the past decades, photocatalytic technology, has opened a new frontier to harvest solar light for energy conversion and preparation [6]. Later, other metal oxide (e.g., ZnO, Cu$_2$O and WO$_3$) [7–10], metal sulfide (e.g., CdS and MoS$_2$) [11–13], and plasmonic metal (mainly coin metals) based photocatalysts with various nanostructures were found to be active in photocatalysis, rendering the photocatalyst family plentiful and diverse [14–19]. However, the deficiencies, e.g., visible light inertia of TiO$_2$ and other metal oxides due to a wide bandgap, instability of metal sulfides due to self-oxidation, and consequently, the apparent quantum efficiency (AQE) remains to be the central task in the fledgling yet rapidly evolving field.

Titanium dioxide (TiO$_2$), as a pioneering material in photocatalytic technology, has opened a new frontier to harvest solar light for energy conversion and preparation [6]. Later, other metal oxide (e.g., ZnO, Cu$_2$O and WO$_3$) [7–10], metal sulfide (e.g., CdS and MoS$_2$) [11–13], and plasmonic metal (mainly coin metals) based photocatalysts with various nanostructures were found to be active in photocatalysis, rendering the photocatalyst family plentiful and diverse [14–19]. However, the deficiencies, e.g., visible light inertia of TiO$_2$ and other metal oxides due to a wide bandgap, instability of metal sulfides due to self-oxidation, and...
secondary pollution of transition metals because of metal leaching, hamper their further developments. Graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) is a metal-free polymeric semiconductor, which has become a rising star since its photocatalytic capability for water splitting was reported in 2009 [20]. Its versatile merits including unique electronic band structure, superior thermal and chemical stabilities, easy preparation and functionalization [21–24], as well as an excellent visible light response with a narrow band gap (~2.7 eV) make carbon nitride-based photocatalysis explosively developed in the past decade.

Nevertheless, the development of state-of-the-art carbon nitride photocatalysts was constrained by a low apparent quantum efficiency (AQE), due to the weak response ability at long wavelengths of light, shallow depth of photon penetration and fatigue charge carriers for the short diffusion length. In contrast, two-dimensional (2D) g-C\textsubscript{3}N\textsubscript{4} nanosheets with atomically layered structure exhibit unique merits: 1) a higher surface area for more active sites; 2) an ultrathin structure with a short diffusion length for hot carriers; and 3) red shifted light absorption by less layers for more light harvesting [25–27]. Whereas, fast recombination of photogenerated electrons and holes in a few femtoseconds to nanoseconds remains [27,28]. The sluggish charge carriers in 2D carbon nitride based photocatalysis stem from the weak static internal electric field (IEF) along the highly symmetric unit cells of 2D carbon nitride and vulnerable dynamic electric field force in photocatalysts. In recent years, dynamic electric fields based on piezoelectric, pyroelectric, or triboelectric effects have been proposed and received significantly improved charge dynamics for catalysis. However, the dynamic electric field always relies on external energy consumption (i.e., thermal and mechanical energy) despite of the higher acceleration of charge separation and transfer than static internal electric field [29–32].

A static IEF is the inherent physical field within a carbon nitride based photocatalyst, and acts as a pump to expedite the migration of charge carriers. Once the driving force on charge carriers fails to overcome the stronger constraint of the Coulomb force, they would decay in the forms of radiative and non-radiative recombination, resulting in unsatisfactory performances. Fabrication of heterostructure is an effective strategy to build static IEF owing to the different work functions from each counterpart. Photoexcited charge carriers would be energized to be quickly separated and transferred for targeted redox reactions with the assistance of the electric field force at the interface of heterostructures [33–35]. 2D g-C\textsubscript{3}N\textsubscript{4} nanosheets are beneficial for the accommodation of other hybrids and engineering of the contact area, attributing to the high surface area of thin nanostructure. Therefore, a myriad of 2D carbon nitride-based heterojunctions with different types, e.g., type II, Z-scheme and S-scheme heterojunctions, have been acquired. Although different types of carbon nitride-based heterojunctions for better light harvesting efficiency have been summarized in previous works, the inherent driving force of heterostructures on charge carriers has yet been brought to the forefront, which is the determining factor on charge dynamics. Therefore, a timely overview on the recent progress of IEF driven photocatalysis is highly desirable, not only to unveil the basic working mechanism, but also to inspire future research directions in 2D carbon nitride-based heterojunctions.

In this work, we illuminate the dominating effect of IEF on charge carriers in 2D carbon nitride-based heterojunctions, and elaborate IEF modulation for versatile applications (Fig. 1). Firstly, the fundamental of IEF in various types of 2D g-C\textsubscript{3}N\textsubscript{4} based hybridizations is introduced, followed by the elucidation of the interfacial effect of heterojunctions on IEF. Emphasis will be put on the IEF modulation enabled by dimensional engineering of a guest on a 2D g-C\textsubscript{3}N\textsubscript{4} host, i.e., point (0D/2D), line (1D/2D), surface (2D/2D) contact and bond connections (in-plane heterojunction). In addition, the cutting-edge approaches for IEF monitoring including theoretical calculation and advanced characterization techniques are summarized. Subsequently, progresses of IEF driven photocatalysis in an array of applications, including water splitting, carbon dioxide reduction, and pollutant degradation, are systematically reviewed. Last but not least, perspectives of IEF driven photocatalysis in carbon nitride-based heterojunctions are elucidated, aiming at exploring more efficient photocatalysts for solar energy conversion. It is anticipated that this review can deliver new insights into the fundamental and engineering of IEF in carbon nitride-based photocatalysis and further accelerate the development of this important research area.

2. Fundamentals of photocatalysis with carbon nitride-based heterojunctions

2.1. Basic principles of photocatalysis

In a heterogeneous photocatalytic process, solar energy can be ultimately stored into chemical fuels when a photocatalyst is irradiated under sunlight. A typical photocatalytic reaction mainly undergoes three stages: (1) photon with equal/higher energy to than the bandgap of a photocatalyst will excite the electrons to jump from valence band (VB) to conduction band (CB), leaving positive holes at VB; (2) photoexcited charge carriers will be separated and migrated to the surface of the photocatalyst to initiate redox reactions; (3) hot electrons will eventually participate into reduction reactions, such as CO\textsubscript{2} reduction.

![Fig. 1. Schematic illustration of IEF on 2D C\textsubscript{3}N\textsubscript{4} hybrids and its fabrication, modulation and application.](image-url)
and water splitting reactions, while hot holes are involved into oxidation processes, including photodegradation and water oxidation reactions. However, photoexcited electrons and holes are easy to be recombined once their dynamics is not strong enough, leading to unsatisfactory photocatalytic efficiency. Therefore, continuous efforts are highly desired on steering directional charge dynamics for fast separation and migration of photogenerated electron-hole pairs.

### 2.2. 2D g-C\(_3\)N\(_4\) materials

g-C\(_3\)N\(_4\) has attracted considerable attention owing to its splendid properties of facile accessibility, visible light harvesting and environmental friendliness. However, several fatal deficiencies co-exist on bulk g-C\(_3\)N\(_4\), such as a low specific surface area, weak visible light response and fast charge recombination rate. Usually, 2D materials exhibit unique properties in photocatalysis, such as a quantum confinement effect, a visible light response ability, tunable energy levels, a superior charge transport and a high surface area. As such, 2D carbon nitride nanosheets have been widely selected as benchmark photocatalysts in versatile photocatalytic applications [36].

Yang et al. innovatively prepared ultrathin 2D g-C\(_3\)N\(_4\) nanosheets by a liquid phase exfoliation strategy [37]. The resultant g-C\(_3\)N\(_4\) nanosheets not only retain the properties of bulk carbon nitride, e.g., a stoichiometric N/C ratio, but also acquire some unique superiorities including a thickness of 2 nm in isopropanol solution, abundant reactive sites with a high surface area as well as accelerated separation and transportation rates of charge carriers. 2D g-C\(_3\)N\(_4\) is considered to possess higher potentials than bulk carbon nitride for solar energy harvesting, thus its synthesis approaches are continuously upgrading. A typical top-down strategy imitating the preparation of graphite oxide was employed to generate high-quality 2D carbon nitride nanosheets. For example, Xu et al. fabricated g-C\(_3\)N\(_4\) nanosheets based on the classical Hummers’ method, where a concentrated H\(_2\)SO\(_4\) (98%) exfoliation approach coupled with water dilution was involved [38]. In this process, H\(_2\)SO\(_4\) functioned as a scissor to destroy the hydrogen bond within the layers of bulk g-C\(_3\)N\(_4\) and some intralayer –NH– groups, finally decomposing bulk g-C\(_3\)N\(_4\) into small pieces. Considering incorporation of an acid in the preparation process makes the method complex and hazardous, Niu et al. developed a thermal oxidation etching strategy to prepare g-C\(_3\)N\(_4\) nanosheets from the parent bulk g-C\(_3\)N\(_4\) [39]. The mechanism of this method is to gradually break the interlayer hydrogen bond in a hot air oxidation process, so that the thickness of bulk g-C\(_3\)N\(_4\) is reduced to the desired nanoscale. The resultant nanosheets possessed a large surface area owing to the ultra-thin nanostructure, which improved the electron transport ability along the in-plane direction and a prolonged lifetime of charge carriers, resulting in superior photocatalytic activities under solar light irradiations.

Although 2D carbon nitride exhibits superb photocatalytic capability and enhanced light harvesting after the bulk structure is exfoliated to nanosheets, its large-scale production is still impeded by the dissatisfactory AQE, attributing to the underpowered charge carriers. As such, a myriad of 2D carbon nitride-based heterojunctions have been synthesized to build IEF. In the following sections, emphasis will be put on IEF fabrication in different types of 2D carbon nitride-based heterojunction and IEF optimization by interfacial engineering.

### 2.3. IEF in 2D carbon nitride-based heterojunctions

IEF poses an inherent driving force on photo-excited charge carriers of a photocatalyst. However, the intrinsic IEF for the highly symmetric 2D carbon nitride is negligible, which leads to a rapid recombination rate of photo-generated charge carriers. Breaking the symmetry could alter the charge distribution of carbon nitride to generate an induced interfacial IEF [40]. For instance, construction of appropriate 2D carbon nitride-based heterojunctions is one of the most effective strategies to build and engineer IEF at the junction or interface owing to the different work functions of each counterpart. The difference of band structures (conduction and valance bands) at the interface of heterojunction imposes an electric field force on charge carriers to improve their charge dynamics and outputs in redox reactions after irradiated by sunlight. Meanwhile, fabrication of a heterojunction is always accompanied with enhanced light absorption by coupling with a lower bandgap semiconductor and reduced redox overpotentials by addition of extra active sites. Therefore, the efficiency of photocatalytic reactions can be remarkably increased. In the following sections, we will elucidate various types of heterojunctions in terms of the progression of the heterojunctions, including type II, Z-scheme, S-scheme, and Schottky heterojunctions (Fig. 2).

#### 2.3.1. S-scheme heterojunction

Type II heterojunction is first proposed by aligning two semiconductors (denoted as PS1 (right) and PS2 (left)) with staggered band structures [41]. In a type II heterojunction system, the CB position of PS1 is higher than that of PS2, while the VB position of PS2 is deeper than that of PS1, resulting in the accumulation of electrons at the CB of PS2 for a reduction reaction and gathering of hot holes at the VB of PS1 for an oxidation reaction (Fig. 2a). Nevertheless, type II heterojunctions bear some drawbacks including irreconcilable resistance for charge transfer and weakened redox capabilities [42]. A Z-scheme photocatalyst is thus explored, and is generally divided into traditional Z-scheme, all-solid-state Z-scheme and direct Z-scheme heterojunctions [43,44]. Recent investigations also indicated that the electron transfer mechanism of type II, traditional Z-scheme photocatalysts and all-solid-state Z-scheme photocatalysts is wrong [35,45]. Although direct Z-scheme heterojunction without intermediates in construction of an internal electric field was further introduced to clarify the mistakes of traditional type II heterojunctions [44] (Fig. 2b), its inherent charge transfer mechanism was not explored and validated in depth.

To better integrate and explain the charge transfer mechanism of direct Z-scheme heterojunction, Yu et al. innovatively brought forward the concept of an S-scheme heterojunction [35]. An S-scheme heterojunction is dependent on the synergism of a reduction photocatalyst (RP/PS1) and an oxidation photocatalyst (OP/PS2) with staggered band structures, which are similar to the type II heterojunction but totally different in the separation pathway of electron-hole pairs (Fig. 2c). In S-scheme heterojunctions, the powerful photogenerated electrons and holes are preserved in the higher CB of PS1 and lower VB of PS2, respectively. Meanwhile, the pointless electrons and holes are recombined, rendering a strong redox potential as well as high charge separation and transfer efficiency. In general, the Fermi level, CB and VB positions of PS1 are higher than those of PS2 to make sure that the electrons in the PS1 continuously migrate to PS2 till the Fermi level is offset. When the two photocatalysts are in contact, the diffusion of free electrons creates an IEF directing from PS1 to PS2 with band bending until the Fermi energy aligns to the equilibrium simultaneously. Upon light irradiation, the photo-excited electrons at the CB of PS2 will migrate to the VB of PS1 to recombine with the holes rapidly while partially transferred electrons would be further excited to CB of PS1 with a stronger reducing power [35,43,45]. The three factors, including IEF, band bending and Coulombic attraction, constitute the main driving forces for the separation and migration of charge carriers at the interface. Consequently, the inferior electrons and holes are eliminated, while the photogenerated electrons and holes with high redox abilities are ready to participate in surface reactions. As a result, an S-scheme heterojunction inherits the band structure of type II heterojunction and the charge-diffusion pathway of an all-solid-state Z-scheme system, resulting in superior separation efficiency of electrons and holes while simultaneously remaining strong redox potentials. Furthermore, an S-scheme heterojunction retains the preponderance on IEF and band bending force over type II and Z-scheme heterojunctions. The novel concept has been beneficial for mainstream photocatalytic reactions such as water splitting to H\(_2\), CO\(_2\) reduction and pollutant degradation.
2.3.2. Schottky heterojunction

In addition, 2D g-C₃N₄ could accommodate noble metal nanoparticles (NPs), whose surface plasmon resonance (SPR) effect leads to an enhanced electric field at the contact interface [51]. Therefore, it is of necessity to elucidate the mechanism of metal NPs/2D g-C₃N₄ Schottky heterojunctions (Fig. 2d). When a metal NP is loaded on a 2D g-C₃N₄ nanosheet, an energy barrier difference (denoted as the Mott-Schottky barrier) is produced at the contact interface originated from the distinct work functions between the metal and carbon nitride, which facilitates the diffusion of photoexcited electrons from the CB of g-C₃N₄ to the Fermi level of metals and thus prevents the recombination of electron-hole pairs [52,53]. Moreover, a photothermal effect co-exists in Schottky heterojunctions that can ameliorate the visible light conversion and charge carriers’ utilization efficiency.

Overall, IEF can be easily fabricated at the interface of various 2D g-C₃N₄-based heterojunctions to vitalize the fatigue charge carriers in highly symmetric carbon nitride. Nevertheless, the fatal deficiencies of type II, Z-scheme and Schottky heterojunctions impede their further improvements. For instance, the enhanced charge dynamics in type II heterojunction is at the cost of redox abilities, and metal is indispensable in Z-scheme and Schottky heterojunctions. Alternatively, the charge dynamics of the emerging S-scheme heterostructure is remarkably enhanced, and the strong redox capabilities are retained. As a result, this fledgling but promising structure demands further in-depth researches for more highly efficient 2D g-C₃N₄-based photocatalysts.

2.4. IEF controlling via interfacial engineering

The nature of a guest on carbon nitride nanosheets determines the type of heterojunction and the location of IEF within band structures, while interfacial engineering dominates the IEF intensity, maximally promoting the charge dynamics for a high photocatalytic throughput. In the following section, interfacial engineering strategies including accommodation of different dimensional (0D, 1D and 2D) hybrids and hybridization with different contact patterns (van der Waals interaction and bond connection) will be reviewed in detail, and the resultant influences on IEF and charge dynamics of 2D g-C₃N₄-based heterojunctions will also be discussed.

The interfacial IEF is pivotal to accelerate the separation and migration of photo-excited carriers for better photocatalytic activity and stability in binary or multiple heterojunction systems [54–56]. According to the space charge region theory in p-n heterojunction, the diffusion motion of the free electrons and the drift motion of the internal electric field generate a limited charge region inside the heterojunction, which is composed of uncompensated ionized impurity charges [57]. The larger area of the space charge region is, the more photo-excited carriers in the heterostructure are separated at interface and transferred to suitable sites [58]. Besides, it is reported that heterojunctions experiencing different interfacial modifications demonstrate varying reaction pathways. For instance, Gu et al. fabricated a Bi₂S₃/g-C₃N₄ p-n
heterojunction with different functional groups (i.e., -COOH, -N-(C)$_3$ and -C-N-H) at the interface for bisphenol A (BPA) removal [57]. A type II charge transfer mechanism was achieved on pristine Bi$_2$S$_3$/g-C$_3$N$_4$ without •O$_2$. Whereas, enhanced IEFs were realized on the functionalized Bi$_2$S$_3$/g-C$_3$N$_4$. Noticeably, a different reaction mechanism occurred in BPA removal by •O$_2$ as the main ROS. As a result, interfacial engineering is a valid approach to control the IEF of heterojunction catalysts, leading to red-shifted light absorption, accelerated separation and migration rates of electron-hole pairs and finally elevated photocatalytic performances.

As summarized in Fig. 3, the interface of 2D g-C$_3$N$_4$ nanosheet based heterojunctions can be classified into inter-plane and intra-plane interfaces, where the former can be engineered via hybridization of 2D g-C$_3$N$_4$ with different dimensional (0D~2D) photocatalysts in a vertical direction, while the latter exists in a 2D–2D in-plane heterojunction bonded along a lateral direction [59–63]. The effects of the contact pattern and interfacial interaction on the formed IEF and charge dynamics will be elaborated in the following sections.

3. IEF in different dimensional guests/C$_3$N$_4$ nanosheets interfaces

The surface of 2D carbon nitride nanosheets is dangling-bond-free, as such, hosting other dimensional (0D, 1D, and 2D) materials on 2D g-C$_3$N$_4$ avoids a rigorous lattice-matching that is highly required on the fabrication of covalent crystal-based hybridizations. Various strategies have been implemented on 2D carbon nitride nanosheets to accommodate other photocatalysts for heterojunctions. Meanwhile, the large surface area of 2D carbon nitride nanosheets is favorable to laterally and vertically engineer the contact between carbon nitride and other hybrids. IEF is thus enhanced at the interface of 2D g-C$_3$N$_4$-based heterojunction, which drives charge carriers to separate and transfer for an

![Fig. 3. Graphical illustration and typical SEM images of different contacts in 2D carbon nitride-based heterojunctions.](a) Point-contact of carbon sphere/g-C$_3$N$_4$ composite. Reproduced with permission [59]. Copyright 2022, Elsevier. (b) Line-contact of W$_{18}$O$_{49}$/g-C$_3$N$_4$ composite. Reproduced with permission [60]. Copyright 2021, Elsevier. (c) Face-contact of Ti$_3$C$_2$/g-C$_3$N$_4$ composite. Reproduced with permission [61]. Copyright 2020, Elsevier. (d) Interface of graphene/carbon nitride in-plane composite. Reproduced with permission [62]. Copyright 2020, ACS Publications.)
improved photocatalytic performance. Integration of carbon nitride with different dimensional guests for various 2D g-C3N4-based heterojunctions (i.e., 0D/2D, 1D/2D and 2D/2D) is an effective approach to control the size of charge transferring channel and is beneficial for the IEF optimization. Meanwhile, the different interactions between each counterpart of heterojunction pose different effects on charge carriers’ separation and mobility. Besides, 2D carbon nitride nanosheets with terminal groups are conducive to epitaxially growing with other lattice-matching photocatalysts for in-plane heterojunctions. The charge carriers would be rapidly separated and transferred once excited at the special junction. More significantly, the energy loss can be avoided in the absence of interface in the novel heterojunction. Therefore, the perfect heterojunction in the structure will be introduced and its effect on IEF will be discussed.

3.1. 0D/2D carbon nitride heterojunction

Zero dimensional nanostructured materials, such as 0D nanoparticles and quantum dots, exhibit strong light-matter interactions and tunable optical properties due to their quantum confinement effects [64]. The larger contact areas of 2D carbon nitride nanosheets can prevent the aggregation of 0D nanomaterials [63], and 0D/2D carbon nitride composites have been widely fabricated.

Noble metals, e.g., Au, Ag and Pt, exhibit a strong SPR effect under light irradiation, and thus can efficiently capture photoexcited electrons to suppress their recombination with hot holes. Noble metal-based nanoparticles and quantum dots are commonly loaded on 2D carbon nitride as co-catalysts. Compared with noble metal composites, non-noble metal based compounds, such as TiO2 [50], Co3O4 [16], Ni2P [17], CdS [18], etc. are less expensive, and their 0D nanostructures have attracted surging interest to decorate 2D g-C3N4. A built-in electric field at the metal-C3N4 interface is induced to enhance the dynamics of hot carriers and improve the photocatalytic capacity of 2D g-C3N4, ascribed to the different work functions between metal nanoparticles and carbon nitride. The resultant IEF effectively hampers the recombination and promotes the transportation of charge carriers in g-C3N4. However, the utilization of metals results in a secondary contamination due to metal leaching.

In the past decades, green catalysis with metal-free photocatalysts have drawn considerable attention. Sun et al. found that the size and photocatalytic performance of g-C3N4/carbon nanospheres (GCN-CS) could be tuned by controlling the hydrothermal temperature and duration [19]. The interfaces between g-C3N4 and carbon nanospheres would induce IEF to increase the separation rate of photogenerated electron/hole pairs (Fig. 4a). A proper size of CS (200–500 nm) balanced the faster electron transfer and the lower recombination within IEF, achieving an optimized photocatalytic performance. To further unveil the effect from the chemical environment of CS on IEF at point contact, Sun et al. subsequently loaded uniform nitrogen-doped carbon nanospheres (NC) onto GCN (Fig. 4b) [65]. N doping would extend the...
absorption edges of GCN to the visible light region for higher light harvesting efficiency, and significantly enlarge IEF to defer the recombination rate of electron-hole pairs, thus remarkably enhancing the photocatalytic performance of NC/GCN composites in sulfachloropyridazine degradation (Fig. 4c).

In total, 0D/2D nanostructure exhibits improved solar light absorption and an enhanced IEF at the point contact for higher photocatalytic activities. In the meantime, the unique properties of 0D materials, e.g., quantum effect and SPR effect, render another enhanced IEF on the surface of 0D nanoparticles. However, either the point contact or the surface of 0D materials is the reactive site of a specific photocatalytic process [66]. Therefore, it is necessary to distinguish the active sites on 0D/2D nanostructures, which would be conducive to maximizing its light harvesting efficiency and photocatalytic throughput by interfacing engineering.

3.2. 1D/2D carbon nitride heterojunction

1D nanostructure mainly includes nanotubes, nanoribbons and nanowires. Compared with point contact in 0D/2D heterostructure, a line contact in 1D/2D composites could provide a relative larger IEF channel for quick separation and movement of charge carriers. Therefore, 1D/2D heterojunction is another intriguing nanostructure to assemble contact interface and engineer IEF, thereby improving the photocatalytic performances.

Till now, 1D carbon nanotubes [71], NaUnaO3 nanowires [72] and CdS nanorods [73] have been loaded on g-C3N4 nanosheets to form intimate interfaces (parallel 1D on 2D, Fig. 4). Carbon nanotubes (CNT) have received considerable enthusiasm for fabrication of 1D/2D heterostructure owing to its excellent electrical conductivity and unique hollow structure [68–70]. Ma et al. combined g-C3N4 nanosheets with multi-walled carbon nanotubes into a 3D porous composite by π-π stacking and electrostatic interactions (Fig. 4f) [69]. The addition of CNT endowed the prepared photocatalyst with a large surface area, improved charge separation and transportation abilities. Compared with the van der Waals interaction between defect-free CNT and g-C3N4 nanosheet, functional CNT is more conducive to integrating with g-C3N4 and facilitating electron transfer [74]. Based on this, Zhao et al. modified g-C3N4 nanobelts (CNN) with hydroxyl modified CNT (HCNT) via combined solvothermal and ultrasonic methods to improve the photocatalytic performances in both tetracycline hydrochloride (TC) degradation and H2 evolution (Fig. 4g) [70]. The introduction of HCNT facilitated the separation of photo-generated electron-hole pairs as well as improved the visible light harvesting efficiency. Although the introduction of HCNT decreased the surface area and pore volume of the HCNT/CNN composite, its high conductivity, electron storage capacity, high electron trapping ability and low Fermi level dominate the photocatalytic performance (Fig. 4h). Besides, the formation of hydrogen bonds between HCNT and CNN can also facilitate the electron transfer from the CNN to the HCNT surface. In addition, single wall carbon nanotubes (SWCNT) exhibiting the non-resonant plasmonic effect were also integrated with 2D g-C3N4 (Fig. 4d–e) [68]. The unique structure induced an enhanced IEF at the contact, creating faster charge migration and separation with prolonged lifetimes of hot carriers. As such, the novel metal-free photocatalyst achieved an efficient photocatalytic performance in the overall water splitting reaction.

As the interface of heterojunction determines the separation and transfer of photogenerated electron-hole pairs, a 1D–2D structure with multi-interface has been applied to improve the photocatalytic activity. Specifically, Huo et al. loaded rod-like CeO2 (R-CeO2) and reduced graphene oxide (rGO) on the surface of g-C3N4 nanosheets by an ultrasound and hydrothermal approach to construct a 1D–2D sandwich photocatalyst for CO2 reduction. The interesting structure provides abundant diffusion channels to improve the electron transfer efficiency [75]. Therefore, the yields for CO and CH4 of the rGO/R-CeO2/g-C3N4 photocatalyst were about 4 and 6 times higher than those of pure g-C3N4, respectively.

Overall, IEF of 1D/2D carbon nitride-based heterojunction varied with the fabrication strategy, contact interface and decorations with functional groups. As a consequence, substantial effort on interfacial controlling is still demanded to maximize IEF for rapid charge dynamics and satisfied photocatalytic performances. 3D network of aerogel with abundant pore structures and huge specific surface areas can provide abundant contact areas and efficiently absorb the reactants [76]. Therefore, embedding the fabricated 1D–2D heterojunction onto the unique 3D aerogel network is more promising for the practical applications.

3.3. 2D/2D carbon nitride heterojunction

2D/2D heterojunction presents a larger contact area than the point and line contacts in 0D/2D and 1D/2D heterojunctions, respectively. Owing to the intimate surface-to-surface interface of 2D/2D structure, an enhanced IEF can be induced and can provide more separation channels and reduce the internal transfer resistance with shortened transfer distance for photoinduced charges. Meanwhile, the largest interface possesses abundant catalytic active sites and enhanced light absorption ability, which can dramatically improve the light harvesting and photocatalytic throughputs.

Till now, many approaches have been proposed to prepare 2D/2D g-C3N4 heterojunction, including in-situ, ex-situ and top-down fabrication methods. The “ex-situ” method for preparation of 2D/2D g-C3N4-based heterojunctions is on the basis of pre-synthesis of 2D nanomaterials and 2D g-C3N4 nanosheets. Then the 2D/2D g-C3N4 heterojunctions are formed by hydrothermal, solvothermal, microwave, self-assembly and other approaches. For example, Li et al. prepared LaVO4/g-C3N4 heterojunctions by a self-assembly method, where the square LaVO4 nanoflakes were tightly anchored on the surface of thin-layered g-C3N4 nanosheets [77]. Specifically, g-C3N4 nanosheets and LaVO4 nanoflakes were acquired via in-situ self-assembly process (Fig. 5a). The prepared LaVO4/g-C3N4 heterojunction enables a H2 evolution rate by 3-fold higher than that of g-C3N4 with a high furfural production rate of 0.95 mmol g−1 h−1.

The interaction between counterparts of heterojunction is always the weak van der Waals force, and an in-situ growth method for heterojunction with intimate contacts has been proposed. One component is pre-synthesized as a substrate and then another component directly grows on the substrate surface through one-step growth or multi-step conversion process. Zhang et al. prepared a 2D/2D TiO2/g-C3N4 heterostructure via in-situ growth of ultrathin 2D-TiO2 on g-C3N4 nanosheets (Fig. 5b) [78]. This method allowed the nanosheets to form strong chemical bonds during the self-assembly. This tightly coupled 2D/2D TiO2/g-C3N4 interface exhibited unique chemical states and electronic structures for a robust interlayer charge transfer. A yield of 80% has been achieved by the obtained heterojunction for visible-light benzyl amine coupling reactions, which is superior to either g-C3N4 or 2D-TiO2 photocatalyst. The significant enhancement can be ascribed to the adequate separation of photo-generated electrons driven by the strong IEF at the tightly coupled 2D/2D heterojunction interface.

Heterojunctions prepared via in-situ or ex-situ strategies are always confronted with low repeatability. Zhang et al. developed a top-down exfoliation method to prepare a 2D/2D g-C3N4 van der Waals (VDW) homojunction (Fig. 5c) to boost the charge mobility for enhanced photocatalytic activities [79]. Bulk g-C3N4 was exfoliated firstly to g-C3N4 nanosheets, which were then calcined under CH4 gas. The pyrolysis of CH4 molecules produced carbon radicals to attack and replace the nitrogen atom in g-C3N4 matrix to form carbon-rich g-C3N4. Consequently, a sandwich nanostructured VDW heterojunction, consisted of in situ formed 2D carbon rich g-C3N4 and 2D g-C3N4 nanosheets, was assembled. Compared with 2D/2D g-C3N4 VDW heterojunctions prepared through a bottom-up method, the heterojunction prepared by a top-down strategy was more uniform, defect-free and robust. The
Exfoliation to nanosheets could acquire higher capability for radiation harvesting due to the increased specific surface area and enhanced electric field. Meanwhile, the VDW heterojunction exhibited stronger radiation absorption and extended the solar response towards the longer wavelength range. As such, the photocatalytic performance of the prepared heterojunction was improved by 8.6 folds than that of g-C$_3$N$_4$ in water splitting reaction to hydrogen.

In addition, other methods such as direct calcination of precursors [61] have also been implemented to fabricate 2D/2D g-C$_3$N$_4$-based heterojunctions. Yang et al. prepared an ultrathin 2D/2D Ti$_3$C$_2$/g-C$_3$N$_4$ heterojunction by calcination of the bulk Ti$_3$C$_2$ and urea mixture via NH$_3$ erosion [61]. Urea was used as the gas template and g-C$_3$N$_4$ precursor to exfoliate Ti$_3$C$_2$ into nanosheets and to craft Ti$_3$C$_2$/g-C$_3$N$_4$ heterojunction (Fig. 5d). Different from the in-situ method, pre-synthesis of one component as a substrate is dispensable in the direct calcination method. The as-prepared heterojunction showed enhanced CO$_2$ photoreduction activity and the total CO$_2$ conversion is higher by 8.1 times than that of pure g-C$_3$N$_4$. These improvements are mainly attributed to the enhancements on CO$_2$ adsorption and activation, and the intimate contact of 2D/2D Ti$_3$C$_2$/g-C$_3$N$_4$ ultrathin heterojunction to stimulate an efficient spatial separation of photo-excited charge carriers.

Moreover, it is worth noting that the materials that combined with 2D g-C$_3$N$_4$ for heterojunction experience from the traditional based semiconductors, TiO$_2$ [78], Fe$_2$O$_3$ [80], SnS$_2$ [81], to the emerging metal free materials, such as graphdiyne (GDY) [82]. GDY as a new 2D semiconductor consisting of sp and sp$^2$ hybridized carbons, exhibiting superior electron and hole mobility rates [83]. In addition, GDY has similar π-conjugated structure and valence band position to g-C$_3$N$_4$. Thus, 2D GDY and g-C$_3$N$_4$ can interact to form an ultrathin 2D/2D GDY/g-C$_3$N$_4$ heterojunction through π–π stacking. Han et al. initially conceived and obtained the unique 2D/2D GDY/g-C$_3$N$_4$ heterojunction, which offered a large face-to-face interface and a short distance for photo-induced holes to transfer from g-C$_3$N$_4$ to GDY [82]. The abundant IEF mediated channels in the prepared heterojunction and the high hole mobility of GDY can rapidly accumulate hot holes at GDY side to suppress the recombination of photocarriers in g-C$_3$N$_4$. Therefore, the 2D/2D GDY/g-C$_3$N$_4$ heterojunction exhibited excellent photoelectron-catalytic performance in water splitting.

Overall, 2D/2D carbon nitride heterojunction is a photocatalyst that is easy to be synthesized but hard to be perfect. Most reported 2D/2D carbon nitride heterojunctions are mainly dependent on the bottom-up method. As such, exploitation of more epitaxial growth methods for 2D/2D carbon nitride VDW heterojunction is highly demanded. Besides, hybridization of 2D carbon nitride with high-performing 2D materials for giant IEF and superb photocatalytic performances is a future direction.

3.4. IEF along carbon nitride in-plane heterojunction

Recombination of photogenerated carriers and energy loss will
inevitably occur at the contact space region of 0D/2D, 1D/2D and 2D/2D carbon nitride-based heterojunctions owing to the restriction of the weak van der Waals force and surface barrier. Consequently, it is of necessity to delocalize the photogenerated carriers with the assistance of a giant intralayer asymmetric driving force and accurately pilot regular transfer of photo-excited carriers to reactive sites [84]. Recently, in-plane heterojunction based on graphene, ultrathin 2D noble metal nanostructures and layered transition metal dichalcogenides (TMDs) have shown great prospects in optoelectronic devices, such as transistors and photodetectors [85–89]. For instance, Gong et al. prepared an in-plane WS\(_2\)/MoS\(_2\) heterostructure with sharp zigzag interface, which provides an excellent platform to tune the band structure and electronic properties [90]. Researches on in-plane junction showed that a strong IEF was induced at the non-contact bonding interface, navigating and driving photo-generated electrons and holes to corresponding redox sites with a less energy loss. Inspired by this, 2D g-C\(_3\)N\(_4\) nanosheet with similar hexagonal structure to that of graphene has attracted extraordinary enthusiasm for fabrication of in-plane C\(_3\)N\(_4\)/graphene heterojunction in the past decade. An in-plane carbon nitride junction is basically assembled by two or more lattice-matched materials which are connected by terminal functional groups of carbon nitride, and grow along the same lateral orientation of carbon nitride substrate [86,91]. As such, photoexcited electrons could be free to move laterally regardless of the restriction of the third direction. As a result, constructing 2D–2D in-plane carbon nitride-based structure is deemed as a promising strategy to address the intrinsic bottlenecks of pristine carbon nitride, including fast recombination and photo-corrosion of photo-exited carriers confined in the bulk phase, as well as low efficiency of surface transferring and inferior visible light harvesting.

At present, in-plane carbon nitride/graphene heterojunction and in-plane carbon nitride homojunctions are two mainstreams. For the in-plane carbon nitride/graphene heterojunction, the N sites at the edge of the planar tri-s-triazine ring provide abundant lone-pair electrons to connect \(\pi\)-conjugated structured carbon rings [92,93]. The interfacial C-N bonding inclines to capture the photo-carriers and then guide them to active sites for redox processes. Che et al. proposed a 2D carbon ring

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**Fig. 6.** (a) Schematic photogenerated carriers transfer mechanism and structural illustration in (C\(_{\text{ring}}\))-C\(_3\)N\(_4\). (b) Calculated adsorption energy profiles for g-C\(_3\)N\(_4\) and (C\(_{\text{ring}}\))-C\(_3\)N\(_4\) where M refers to surface C sites. (c) Graphical Fermi energy level for pristine g-C\(_3\)N\(_4\), carbon, and (C\(_{\text{ring}}\))-C\(_3\)N\(_4\). Reproduced with permission [94]. Copyright 2017, ACS Publications. (d) The photogenerated electrons transfer pathway of g-C\(_3\)N\(_4\)/graphene in-plane heterojunction, (e) DFT calculation results of g-C\(_3\)N\(_4\)/graphene in-plane heterojunctions and (f) Schematic illustration of the formation of in-plane hetero-structure photocatalyst. Reproduced with permission [62]. Copyright 2020, ACS Publications.
(C$_{3}$N$_{4}$)-C$_{2}$N$_{4}$-based in-plane heterojunction by a thermally π-conjugate bottom-up strategy (Fig. 6a) [94]. For pristine g-C$_{3}$N$_{4}$, oriented charge migration and accumulated electrons around the Fermi energy level are lacking. After coupling the in-plane carbon ring (C$_{3}$N$_{4}$) with the triazine unit of g-C$_{2}$N$_{4}$, a new intermediate energy level is created. The high electron density around the introduced Fermi energy level greatly increases H$_2$O adsorption energy (~1.1 eV) [94] and reduce the intermediate H$^+$ energy barrier formed during photocatalytic water splitting (reduced by 0.49 eV shown in Fig. 6b). Besides, the different work functions between carbon and carbon nitride navigate the separation and movements of electron-hole pairs (Fig. 6c). Accordingly, prolonged lifetimes of photogenerated charge carriers by 10 times than pristine carbon nitride and an elevated quantum yield of 5% at 420 nm are accomplished on the in-plane heterojunction.

However, the bottom-up strategy bears severe drawbacks and the homogeneity of a deposited material in carbon nitride matrix could not be guaranteed [62]. Chemical vapor deposition (CVD) is a classical approach for epitaxial growth of intralayer heterojunction, in which the vapor-phase reactants are decomposed on the solid substrate [86,91]. However, the CVD method requires a high lattice match of each component. Attributed to the minor difference (1.4%) of lattice parameter between carbon nitride and graphene, Zhang et al. fabricated a g-C$_{3}$N$_{4}$/graphene in-plane heterojunction by a top-down hydrogen-initiated chemical epitaxial growth strategy. The novel approach ensured the homogeneity of heterojunction at a relatively low temperature of 500 °C owing to two key factors, namely, the confined spaces and active sites of cyano groups at the edge of porous carbon nitride (Fig. 6f) [62]. The edge of porous carbon nitride confined the movement of generated methane, and the inside cyano group acted as active sites to guarantee the in-situ formation of graphene. The surface plasmon resonance effect (SPR) and high conductivity of graphene resulted in partial metallization and giant built-in electric field at the connection between graphene and carbon nitride, ameliorating the separation of hot electrons and holes (Fig. 6d-f).

Besides, construction of carbon nitride intralayer homojunction is another strategy to rapidly free the charge carriers from the constraint of Coulomb force and drive them to the active sites. Zhang et al. employed a method of homoeptaxial growth along with gas erosion to prepare a carbon nitride homojunction. The different HOMO and LUMO energies for carbon nitride unit cells and that with carbon vacancy provided an intrinsic strong driving force along the in plane of carbon nitride homojunction, which drove photocarriers quickly separated and transferred to catalyst surface [95]. Owing to the increased concentration of carbon vacancies, a higher IEF was acquired. That is to say, the concentration of carbon vacancy dominates the IEF engineering, thus maximizing the mobility and separation of charge carriers.

In total, in-plane carbon nitride-based heterojunctions and homojunctions have demonstrated their high performances in photocatalysis due to the following reasons: (1) fabrication of in-plane heterojunction breaks the symmetry of carbon nitride nanosheets; (2) the different work functions of each component induce giant interfacial IEF at bonding connection to accelerate the separation and mobility of photocarriers; (3) the in-plane driving force plays as a pilot to guide the movements of electrons and holes to reduction and oxidation sites, respectively.

Nevertheless, fabrication of intralayer heterojunction lacks effective approaches. The top-down strategy is suggested to improve the inaccuracy and inhomogeneity of bottom-up strategy. However, carbon nitride is unstable at high temperature with top-down method. Therefore, it is highly desirable to develop a universal and productive technology to fabricate carbon nitride in-plane heterojunction. Moreover, in-plane heterojunctions are restricted by the good compatibility on the lattice constants and lattice symmetry of each component [90]. Accordingly, choosing more lattice-matched components, e.g., boron nitride (BN) material, is another option for the further development of carbon nitride in-plane heterojunction.

In the aforementioned discussion, the IEF optimization of g-C$_{3}$N$_{4}$ based heterojunctions with different dimensions (0D~2D) were well illustrated in Fig. 7. The IEF built in 0D/2D or 1D/2D carbon nitride heterojunctions is closely connected with synthesis strategies, contact interfaces, and functional group decoration. Therefore, interfacial control to maximize the charge kinetics of the IEF and further boost the photocatalytic properties is highly demanded. Heterojunctions with relatively loose contact and low IEF intensity are often achieved via ex-situ approaches including hydrothermal and solvothermal methods, while the in-situ growth and in-situ self-assembly strategies are widely adopted to form heterojunctions with intimate contacts and strengthened chemical bonds between layers for promoted electron transfer with robust IEF. Compared with 0D or 1D materials, 2D/2D carbon nitride heterojunction is easier to obtain with more top-down synthesis methods such as epitaxial growth. The tight and wide contact interface of 2D/2D heterojunction provides a solid foundation to achieve a high-efficiency IEF. Furthermore, the top-down strategy is conducive to the formation of defect-free and uniform VDW heterojunctions and intralayer heterojunctions in 2D/2D carbon nitride composites. However, for the intralayer heterogeneous structures, its development is retarded due to certain compatibility limitations on lattice constants and lattice symmetry of each component, which requires further exploration on selection of appropriate components with effective fabrication approaches. Thus, hybridizing 2D carbon nitride with high-performance 2D materials by virtue of versatile and facile techniques would be a promising and competitive way to favorably modulate IEF for enhanced photocatalytic performance.

4. Strategies for identification of IEF

Up to date, either qualitative or quantitative characterization techniques (Fig. 8) have been adopted to determine IEF, which could be divided into three mainstream categories: (1) Kelvin Probe Force Microscopy (KPFM), Surface Photovoltage Spectroscopy (SPV), Ultraviolet Photoelectron Spectroscopy (UPS) and other photoelectrochemical characterization methods; (2) in-situ characterization technologies including in-situ irradiation X-ray Photoelectron Spectroscopy (ISI XPS), in-situ Electron Spin Resonance (in-situ ESR), in situ Fourier Transform Infrared (in-situ FTIR) and in-situ X-Ray Absorption Spectroscopy (in-situ XAS); (3) theoretical calculations and simulations based on Density Functional Theory (DFT), Finite Element Method (FEM) and finite difference time-domain (FDTD) simulations. Multiple technologies and mathematical simulations have been utilized for accurate detection and scaling of IEF. For example, the KPFM and SPV could reveal the surface potential differences in single crystal or at the interface of two components, and the ISI XPS was adopted to record the charge migration direction. Meanwhile, the work function and Fermi level calculated by DFT could also identify the difference of surface voltage and interfacial charge shift, providing a direct evidence for the formation of IEF.

4.1. KPFM, SPV, UPS and other photoelectrochemical characterization methods

KPFM is rooted from Atomic Force Microscopy (AFM), and used as an effective approach to detect the surface potential distribution and reveal the separation of spatial photo-excited electrons and holes [96]. The principle of KPFM is originated from the difference in electron tunneling abilities of the samples to reflect a relative evaluation or the presence of the IEF. For example, the work function and contact potential of the combination of g-C$_{3}$N$_{4}$ and zinc porphyrin-conjugated microporous polymer (ZnP-CMP) shown in Fig. 8a-b were obtained by KPFM [97]. According to $\Delta V = \Phi - \Phi_{rep}$, $\Phi$ represents the work function of the sample; $\Delta V$ is the contact potential difference (CPD); $\Phi_{rep}$ represents the work function of platinum probe with a value at 5.20 eV [42], the work function of ZnP-CMP (5.82 eV) is smaller than that of g-C$_{3}$N$_{4}$ (5.95 eV). Therefore, the IEF between ZnP-CMP and g-C$_{3}$N$_{4}$ is formed and will result in the transfer of photogenerated electrons flowing from g-C$_{3}$N$_{4}$ to
ZnP-CMP when they are hybridized. According to Kanata’s model, the surface charge density and the surface voltage are two main factors influencing the IEF value [98]. KPFM could be adopted to measure the surface voltage of the samples. However, for calculating the intensity of the IEF accurately, it should be coupled with other characterizations such as Zeta potential, transient photocurrent density and electrochemical measurements [99]. As a relatively accurate method to obtain CPD values as well as related work function of the samples, KPFM method is time-consuming and expensive with a high cost.

Alternatively, SPV is another qualitative approach to be used for validating the presence of the IEF by measuring the surface photovoltage change under the excitation of light illumination [100–102]. The photoinduced electron-hole pairs are immediately separated and transferred by the driving force of IEF, leading to a fast SPV response. Taking a NiCoP/g-C3N4 system as an example, the SPV testing for the surface photovoltage of the NiCoP/g-C3N4 exhibits a stronger photovoltage signal than that of pure g-C3N4 after NiCoP was introduced [99] (Fig. 9c). The SPV results can be attributed to the IEF between g-C3N4 and NiCoP which increased the photogenerated charge carriers and promoted their further migration. It is worth noting that the SPV technology can be integrated with different setups including KPFM. The technology of SPV integrated with the KPFM setup, namely spatial resolution SPV (SSPV), could demonstrate visualized evidence with enhanced spatial and time resolution to detect electronic dynamics and potential distribution of semiconductors [103].

To elucidate possible photocatalytic mechanism of the reactions, work function is a vital factor for determining the Fermi level and band structure as well as validating charge transfer pathway and existence of the IEF. Therefore, UPS measurements are widely selected to record the cut-off edges (E_{cut-off}) to evaluate the work function, flat-band potential and valence band potential. For example, Li et al. obtained the flat band positions and Fermi levels of carbon nitride (GCN) and LaVO4 from Mott-Schottky (M-S) curves, and then further estimated the work functions and valence band (VB) potentials by UPS analysis to comprehensively reveal the electronic structure of the semiconductor [77]. Clearly, the LaVO4/GCN hybrid established Z-scheme heterojunction interfaces with IEF directing from GCN to LaVO4.

Other photoelectrochemical characterization methods are also employed to study the IEF effect on transfer, separation and recombination behavior of photogenerated charge carriers, including Transient Photovoltage Spectroscopy (TPV), Photoluminescence (PL) spectra, Linear Sweep Voltammetry (LSV), and Electrochemical Impedance Spectroscopy (EIS) [48,104–106]. Generally, TPV and EIS are usually adopted to determine the IEF-assisted charge separation and migration efficiency of photo-generated electrons and holes at the interface of heterojunctions. The PL spectra are utilized to characterize the recombination capability of the photoexcited charges via emission peak intensity. Furthermore, the LSV measurements can be performed to estimate the activation barriers and electrocatalytic efficiency of the reduction process after fabrication of IEF in the heterostructure.
the IEF mediated electron transfer pathways, the IEF of ZnIn
in-situ XPS characterization to study the electron transfer behavior at
photogenerated electrons. Additionally, under the known lattice pa-
direction and relative intensity of IEF [105,107,108]. Li et al. conducted
face states of electron accumulation and depletion, reflecting the
parameters, the binding energy of in-situ XPS analysis represents the sur-
nections/holes and hydroxyl radical (•OH) are frequently used as spin trapping molecules to detect elec-
tetra-methylpiperidine-1-oxyl) and DMPO (5,5-dimethyl-1-pyrroline N-
interface of the heterostructure. As shown in Fig. 9 f-g, TEMPO (2,2,6,6-
IEF on the electron transfer efficiency and photocatalytic activity at the
produced in the reaction [77,104,106]. This can be employed to indi-
peaks can be utilized to deduce the specific species of active radicals
aqueous/organic solutions, respectively. Quantitatively, the intensity of
importance of C3N4, In3d and S 2p under dark and 365 nm irradiation. Reproduced with permission [48]. Copyright 2022, Elsevier. The ESR spectra of the as-prepared samples labeled (f) by DMPO for hydroxyl radicals (g) and by TEMPO for e. Reproduced with permission [104]. Copyright 2020, Elsevier.

4.2. ISI XPS, in situ ESR, in situ TEM and others

To further analyze the transient states during a reaction and obtain
the IEF mediated electron transfer pathways, ISI XPS analysis is con-
ducted both in the dark and under ultraviolet irradiation to observe the
binding energy shifts and deduce the possible transfer pathways of
photogenerated electrons. Additionally, under the known lattice pa-
rameters, the binding energy of in-situ XPS analysis represents the sur-
face states of electron accumulation and depletion, reflecting the
direction and relative intensity of IEF [105,107,108]. Li et al. conducted
in-situ XPS characterization to study the electron transfer behavior at
the IEF of ZnInS2/g-C3N4 (ZIS/HCNT) under light irradiation [48]. The binding energy of C 1 s and N 1 s of HCNT exhibits a positive shift, indicating that the photogenerated electrons are transferred from HCNT
to ZIS. Meanwhile, the binding energy of Zn 2p, In 3d and S 2p of ZIS exhibits a negative shift to accept electrons. These results confirm that the formation of IEF promotes the migration of charges with the elec-
tron-accumulated region is formed on the ZIS side and a depletion
region formed on the GCN side. In addition, the electronic structures of
electron-accumulated region is formed on the ZIS side and a depletion
transfer is from GCN to ZIS. Thus, the IEF is established when an

In-situ ESR is another effective technique to determine the effect of
IEF on the electron transfer efficiency and photocatalytic activity at the
interface of the heterostructure. As shown in Fig. 9f-g, TEMPO (2,2,6,6-
tetramethylpiperidine-1-oxyl) and DMPO (5,5-dimethyl-1-pyrroline N-
oxide) are frequently used as spin trapping molecules to detect elec-
trons/holes and hydroxyl radical (•OH)/superoxide radical (•O2)
in aqueous/organic solutions, respectively. Quantitatively, the intensity of
the signal indicates the number of free radicals produced in the photo-
catalytic system. Qualitatively, the area proportion of characteristic
peaks can be utilized to deduce the specific species of active radicals
produced in the reaction [77,104,106]. This can be employed to indi-
rectly reflect the IEF effect on electron transfer efficiency.

Other in-situ characterization technologies including in-situ TEM
[109], in-situ FTIR Spectroscopy [110,111], and in-situ XAS [112,113]
also assist in evaluating and analyzing the transient electron transfer
path, redox states, dynamic atomic structure, ad/desorption changes of
intermediate products, as well as coordination atom shifts induced by
IEF. For instance, in-situ TEM could detect the transient structural
changes of the samples during the reaction; in-situ FTIR could record the
intermediate products generated on the surface of the samples within
the first half-hour reaction, providing a deeper observation for analyzing
the electrons and holes migration through the IEF-driven system.

4.3. DFT and FEM calculations

Except for the above mentioned experimental techniques for deter-
mining the IEF, some theoretical calculation and simulation approaches
such as DFT are also employed to reflect the electronic properties such as
electrostatic potential, work function and differential density based on
the ground-state electron probability density to verify the existence of
IEF theoretically [99]. Tan et al. revealed the interfacial interaction and
charge transfer mechanism of ZIS-x-GCN with DFT calculations [114]. In
Fig. 10a-c, the work function (Φ) of ZIS (Φ = 6.1 eV) is much higher
than GCN (Φ = 4.9 eV), indicating that the direction of electrons
transfer is from GCN to ZIS. Thus, the IEF is established when an
electron-accumulated region is formed on the ZIS side and a depletion
layer formed on the GCN side. In addition, the electronic structures of
GCN, ZIS and ZIS-100GCN were obtained by DFT calculations, which
provided enough evidence for the existence of IEF.

Apart from DFT, other mathematical simulation methods such as
FEM and FDTD have been utilized to evaluate and identify the IEF
strengthened by the LSPR effect and the formation of van der Waals
heterojunction [98]. Wang et al. proved the existence of IEF in 1D car-
bon nanotubes coupled with 2D ultrathin carbon nitride (SWCNT/C3N4)
by FEM simulations [68]. The electrical field distribution in different
wavelengths indicates the extending field enhancement not only at the
interface between SWCNT and C3N4 but also inside C3N4 (Fig. 10d).
Additionally, the generation of Ohmic heat confirmed the conductivity
of C3N4 is lower than that of SWCNT (Fig. 10e). The FEM results reveal
that, below the wavelength of 600 nm, the introduction of SWCNT in-
creases the intensity of IEF on the surface of LSPR structure, facilitating
the fast and direct generation and migration of photo-excited electrons and holes with an enhanced photocatalytic performance. Zhang et al. adopted FEM simulations to describe and explain the enhanced local electric field induced by the LSPR excitation of $W_{18}O_{49}$ on $g$-$C_3N_4$ nanosheets [115]. The LSPR band selections of $W_{18}O_{49}/g$-$C_3N_4$, $g$-$C_3N_4$ and $W_{18}O_{49}$ under monochromatic light (450, 500, 600, 700, 800, 900, and 1000 nm) excitation prove that the elevated intrinsic electric field is closely related to the LSPR absorption band of $W_{18}O_{49}$.

**4.4. Others**

Several effective and practical IEF characterization methods have been summarized above. Besides, other techniques including Raman spectroscopy [116] and AFM [117,118] could also provide information regarding electron density and charge transport ability for measurement of IEF, further proving the elevation of separation and migration of charge carriers driven by the IEF indirectly. Several new emerging characterization techniques have been put forward recently such as SRSPV (spatial resolution surface photovoltage spectroscopy), STEM (scanning transmission electron microscopy) and others [119,120]. They are applied to extract information related to the IEF and the corresponding potential and charge density. Also, the slopes of M-S curves can be utilized to estimate the density dynamics of photo-generated charge carriers.

In conclusion, traditional characterization methods can only reflect the surface states of the samples before and after reaction. Modern in-situ characterization techniques have emerged as useful tools for validating IEF mechanisms by evaluating the transient states during a reaction. However, it is also worth noting that the recorded data from in-situ characterization might be at subtle variance with that from the actual photocatalytic reaction due to the possible change of temperature and pressure. This could be largely minimized and monitored by integrating some photoelectrochemical characterizations, such as M-S curves, UV-Vis DRS, and cyclic voltammetry (CV) curves [108,121]. While, these characterizations still bear some disadvantages: some characterizations are indirect, detecting requirement is strict, and analysis cost is high.

**5. Applications for solar energy conversion**

g-$C_3N_4$ has demonstrated versatile functions in broad fields in the past decade, especially in catalytic fields for energy conversion and environmental purification, owing to its visible light responsive band gap (2.7 eV), suitable band structures with excellent thermochemical stability, high environmental affinity and cost-effectiveness. In the following sections, we mainly focus on the applications of IEF assisted photocatalytic performances in water splitting, carbon dioxide reduction, and pollutant degradation. As shown in Fig. 11, the IEF plays as a pilot by introducing an asymmetric driving force to guide generated electrons and holes moving directly and orderly to the suitable active/reactive sites, respectively.

In photocatalytic reactions, the introduction of IEF could trigger the advanced dynamics of charge carriers on one hand. In the meanwhile, it may also affect the surface reaction features including the adsorption/desorption abilities of the intermediates. Furthermore, we also focus on two main potential differences (PD) as descriptors for quantifying IEF [95], i.e., a interfacial PD (IPD) within 2D g-$C_3N_4$ hybrids, which is the potential difference between the band structures of the two components in the heterojunction, and a band PD (BPD) focuses on the difference between the redox potentials of reactants and the band positions of a semiconductor for actuating charge carriers for photocatalysis. The relationships between the different categories of IEF and photocatalytic performances in various processes will be discussed in detail. It is anticipated that the in-depth mechanism as well as the effects of IEF...
Photocatalytic water splitting is a green and feasible approach to convert solar energy into green hydrogen, which has received significant attention [122]. The water splitting reaction is a reaction with a high energy barrier of the Gibbs free energy of 237 kJ/mol. Thermodynamically, the conduction band potential of a semiconductor material is required to be more negative than the water reduction potential \( E_{\text{H}_2/\text{H}_2O} \), while the valence band potential should be more positive than the water oxidation potential \( E_{\text{O}_2/\text{H}_2O} \). The mechanism of photocatalytic water splitting is as follows: electron-hole pairs can be excited into the conduction and valence bands, respectively. The holes \( h^+ \) migrate to the semiconductor surface and oxidize water molecules to form \( O_2 \), while the electrons \( e^- \) are transferred to reduce \( H_2O \) to \( H_2 \) and \( O_2 \) (1).

\[
2H^+ + 2e^- \rightarrow H_2 \quad (E_0 = 0V)
\]

(1)

\[
H_2O + 2h^+ \rightarrow 2H^+ + \frac{1}{2}O_2 \quad (E_0 = -1.23 V)
\]

(2)

From the equations, it can be inferred that the semiconductor band gap should be greater than 1.23 eV, so that the photocatalytic water splitting can be carried out. But if the energy loss is considered, 2.0 2.2 eV is the suitable forbidden band width for a semiconductor based photocatalyst. Considerable studies have been conducted to configure and engineer the IEF in carbon nitride to energize the sluggish charge carriers and enhance the photocatalytic activity in water splitting.

Ag is a typical plasmonic metal, which was chosen to assist g-C_3N_4 for photocatalytic hydrogen production. 0D Ag quantum dots (QDs) served as effective electron traps after being deposited on g-C_3N_4 and the charge density on both sides of the Ag QDs increased. Another IEF is also formed at the interface of Ag QDs and g-C_3N_4, thus the photogenerated electrons of g-C_3N_4 are transferred to Ag QDs surface to reduce \( H^+ \). However, the high cost and rarity of the precious metals constrain their wide application. It is of great significance to explore green and low-cost systems including transitional metal oxides/sulfides. For instance, Tao et al. [124] successfully constructed 0D/2D heterojunctions comprising of CdS nanoparticles (NPs) and g-C_3N_4 nanosheets (NSs). The enhanced photocatalytic efficiency of this material is mostly due to the close contact interface between CdS and g-C_3N_4 for a type-II charge carrier transfer path. Then the IPD of the system was calculated to be 0.01 eV and the BPD value to be 0.68 eV. Thus, the separation rate of photo-generated electron-pair was enhanced and the photo-corrosion of CdS was avoided.

To intensify the IEF, Liu et al. loaded MoS_2 with various morphologies on g-C_3N_4 nanosheets to form the IEF at a face-to-face and a point-to-face contact, respectively [125-127]. The photogenerated electrons driven by the IEF are gathered on the CB of MoS_2, with the optimal IPD and BPD values reaching 2.09 and 1.77 eV, respectively. The increased IPD dominates a high charge separation rate while the enlarged BPD was favorable for the activation of hydrogen production. Besides, Zhang et al. [128] synthesized a 0D/2D Z-scheme photocatalyst. As illustrated in Fig. 12a, the experimental and DFT calculation results provide strong evidence for the IEF formed by the Z-scheme charge transfer pathway. Heterojunctions with larger contact areas not only provide abundant reactive sites but also enhance electronic interactions through IEF, where the IPD of the system was increased to 1.83 eV and the BPD also reached 1.13 eV.

Line-area contact is another widely adopted approach to build a 2D g-C_3N_4 based heterojunction for boosted photocatalytic hydrogen evolution. Recently, Feng et al. [129] embedded a 1D WO_3 nanotubes (WNT) in the framework of a 2D porous g-C_3N_4 (PCNS). The insertion of WO_3 naturally formed an IEF at its contact with porous g-C_3N_4, accelerating the electron transfer along the one-dimensional channel. Photogenerated electrons in the CB of WNT and holes in the VB of PCNS are rapidly driven by IEF to be separated at the interface, while the electrons accumulated in the CB of PCNS contributed to a high BPD value at 1.49 eV, which promoted the generation rate of \( H_2 \) in photocatalytic water splitting. Furthermore, compared with pure PCNS, there is no significant reduction of \( H_2 \) production after five cycles, revealing the excellent photochemical stability of PCNS/WNT hybrids for photocatalytic hydrogen generation. Similarly, 1D MnO_3/CdO_S was hybridized with g-C_3N_4 to form an IEF, which was verified by the electrochemical tests. The charge separation efficiency was demonstrated to be largely promoted under the IEF [130]. The IPD and BPD reached as high as 2.32 and 1.15 eV, respectively, and both are high enough to drive hot carriers’ participation into redox reactions.

Moreover, heterojunctions with area-area contact are applied for photocatalytic hydrogen production owing to its relatively larger contact interface and charge diffusion channels. Zhang et al. [131] constructed a series of SnS_2/g-C_3N_4 heterojunctions. By adjusting the annealing temperature, the composites can be regulated to achieve different types of charge transfer pathways with various strength of IEF, assisted by transient photovoltage and surface photovoltage techniques. The direction of the IEF and the driving force for charge transfer are proposed. As showed in Fig. 12b, the difference between these two IEFs is mainly related to the difference in work function of SnS_2 processed at various synthesis temperatures.

Heterojunction construction is indeed an effective strategy to build IEF at the interface. However, the defect and disordered interface of the heterojunction could remarkably weaken the strength of the IEF [122, 132]. Based on this, Zhang et al. proposed a hydrogen-induced chemical epitaxy growth strategy and successfully constructed a carbon nitride/graphene intralayer heterostructure photocatalyst [62]. The finite element together with DFT simulation results show that the interface of the constructed intralayer heterojunction exhibits partial metallicity (Fig. 12d), which can effectively improve the visible light absorption. In addition, IEF is significantly enhanced with the increase of graphene content, which accelerates the transfer and separation of photo-generated electrons and promotes electron accumulation.

Hydrogen production is a half-reaction of water splitting, where sacrificial agents such as triethanolamine (TEOA) or methanol are indispensable to consume the hot holes. Compared with photocatalytic hydrogen production, overall water splitting is highly stringent as the requirements for reduction and oxidation processes need to be met.
simultaneously. As such, development of efficient and stable photocatalysts for overall water splitting without sacrificial agents is challenging. Overall water splitting is limited by the sluggish kinetics of the oxygen evolution reaction in the absence of sacrificial agents [134]. To date, considerable studies have proven that the overall water splitting can be achieved without any sacrificial agent by configuring a giant IEF in g-C\textsubscript{3}N\textsubscript{4} [133,135–138]. Specifically, more attention has been paid to metal-free hybrid materials to enhance hydrogen evolution in photocatalytic water splitting. For instance, in a trinary hybrid of g-C\textsubscript{3}N\textsubscript{4}/rGO/PDIP, giant IEF was formed to drive a S-scheme charge transfer that electrons in the CB of PDIP and holes in the VB of g-C\textsubscript{3}N\textsubscript{4} recombine, so that the BPD for reduction in photocatalytic water splitting reaches 0.93 eV and the BPD for oxidation reaches 0.87 eV. As such, the characterization techniques such as chemical impedance spectroscopy and surface photovoltage (SPV) tests verified that the strong IEF formed in g-C\textsubscript{3}N\textsubscript{4}/rGO/PDIP contributed to the reduction of charge transfer resistance and the improvement of charge separation efficiency in photocatalysis (Fig. 12c).

For most reported g-C\textsubscript{3}N\textsubscript{4}-based photocatalysts, the key to enhance photocatalytic water splitting efficiency is to promote the dynamics of photogenerated carriers including excitation, separation, transportation and utilization. Summaries of g-C\textsubscript{3}N\textsubscript{4} as the substrate for interface regulation and construction of IEF in photocatalytic water splitting are listed in Table 1, where IPD and BPD are important descriptors for quantifying IEF at the interface of the heterojunction as well as that between the photocatalyst and the reactants.

To sum up, two noteworthy conclusions can be reached. (1) The heterojunction with an S-scheme or a direct Z-scheme charge transfer always exhibit more advantageous BPD and IPD values than their analogues with a type-II mechanism. The higher BPD/IPD values are beneficial for photocatalytic water splitting to release oxygen and hydrogen. (2) Compared with 1D/2D contact (e.g. g-C\textsubscript{3}N\textsubscript{4}/WO\textsubscript{3} [139]), a 2D/2D contact with the same charge transfer scheme exhibits the highest surface contact, beneficial for the interfacial IEF to promote the separation of photogenerated carriers and diffusion on the photocatalyst surface to participate in redox reactions. Therefore, fabrication of 2D/2D g-C\textsubscript{3}N\textsubscript{4}-based hybrids would be an effective strategy to improve the photocatalytic performance, especially for overall water splitting. Notably, the modification of IEF leads to the enhancement of the structural stability. Although some progresses have been made in the application of g-C\textsubscript{3}N\textsubscript{4}-based photocatalysts in water splitting, the hydrogen evolution and energy conversion efficiencies are far from satisfactory. The comprehensive mechanism and coupling effect in the cascade system for a conclusive role of IEF in escalating the overall reaction efficiency is yet to be fully disclosed.
Table 1
Photocatalytic water splitting over g-C3N4-based photocatalysts for IEF design.

<table>
<thead>
<tr>
<th>g-C3N4 based photocatalysts</th>
<th>Synthesis method</th>
<th>Interfacial effect</th>
<th>Type of Heterojunction</th>
<th>Activity Rate/μmol h⁻¹</th>
<th>IPD (eV)</th>
<th>BPD (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS@g-C3N4</td>
<td>calcination</td>
<td>Point-area contact</td>
<td>Type-II</td>
<td>H2: 73.4</td>
<td>0.01</td>
<td>Re:0.68</td>
<td>[124]</td>
</tr>
<tr>
<td>Pt-Zn-AgIn5S8@g-C3N4</td>
<td>in-situ growth</td>
<td>Point-area contact</td>
<td>Type-II</td>
<td>H2: 346.42</td>
<td>0.48</td>
<td>Re:0.74</td>
<td>[140]</td>
</tr>
<tr>
<td>CeO2@g-C3N4</td>
<td>solvothermal and calcination</td>
<td>Point-area contact</td>
<td>Z-scheme</td>
<td>H2: 203.6</td>
<td>1.83</td>
<td>Re:1.13</td>
<td>[128]</td>
</tr>
<tr>
<td>SbVO4@g-C3N4</td>
<td>physical mixing</td>
<td>Point-area contact</td>
<td>S-scheme</td>
<td>H2: 22.56</td>
<td>1.21</td>
<td>Re:1.63</td>
<td>[141]</td>
</tr>
<tr>
<td>Mn0.5Co0.5S8@g-C3N4</td>
<td>calcination</td>
<td>Point-area contact</td>
<td>S-scheme</td>
<td>H2: 118.1</td>
<td>1.50</td>
<td>Re:1.30</td>
<td>[129]</td>
</tr>
<tr>
<td>Pt-Zn-AgIn5S8@g-C3N4</td>
<td>calcination</td>
<td>Point-area contact</td>
<td>S-scheme</td>
<td>H2: 73.4</td>
<td>0.01</td>
<td>Re:0.68</td>
<td>[124]</td>
</tr>
<tr>
<td>CeO2@g-C3N4</td>
<td>solvothermal</td>
<td>Line-area contact</td>
<td>Type-II</td>
<td>H2: 41.8</td>
<td>0.02</td>
<td>Re:0.59</td>
<td>[143]</td>
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<tr>
<td>WO3/P-g-C3N4</td>
<td>self-assembly</td>
<td>Line-area contact</td>
<td>Type-II</td>
<td>H2: 10.94</td>
<td>1.49</td>
<td>Re:0.72</td>
<td>[129]</td>
</tr>
<tr>
<td>BiS2@g-C3N4</td>
<td>solvothermal</td>
<td>Line-area contact</td>
<td>Type-II</td>
<td>H2: 33.94</td>
<td>1.11</td>
<td>Re:1.36</td>
<td>[144]</td>
</tr>
<tr>
<td>Ni0.85Se@g-C3N4</td>
<td>solvent Evaporation</td>
<td>Line-area contact</td>
<td>Type-II</td>
<td>H2: 175.6</td>
<td>0.89</td>
<td>Re:1.38</td>
<td>[145]</td>
</tr>
<tr>
<td>CoO@g-C3N4</td>
<td>one-pot</td>
<td>Area-area contact</td>
<td>Type-II</td>
<td>H2: 9.67</td>
<td>0.57</td>
<td>Re:0.63</td>
<td>[96]</td>
</tr>
<tr>
<td>Pt-CdS@g-C3N4</td>
<td>hydrothermal</td>
<td>Area-area contact</td>
<td>Type-II</td>
<td>H2: 14.65</td>
<td>0.50</td>
<td>Re:0.60</td>
<td>[146]</td>
</tr>
<tr>
<td>K3H2Nb2O6@g-C3N4</td>
<td>hydrothermal</td>
<td>Area-area contact</td>
<td>Type-II</td>
<td>H2: 17.99</td>
<td>0.69</td>
<td>Re:0.37</td>
<td>[147]</td>
</tr>
<tr>
<td>WO3@g-C3N4</td>
<td>ice template method</td>
<td>Area-area contact</td>
<td>Z-scheme</td>
<td>H2: 15.60</td>
<td>0.84</td>
<td>Re:0.82</td>
<td>[139]</td>
</tr>
<tr>
<td>Mn3S8@g-C3N4</td>
<td>hydrothermal</td>
<td>Area-area contact</td>
<td>Z-scheme</td>
<td>H2: 10.04</td>
<td>1.73</td>
<td>Re:0.74</td>
<td>[148]</td>
</tr>
<tr>
<td>CO3/α-Fe2O3@g-C3N4</td>
<td>solvothermal</td>
<td>Area-area contact</td>
<td>Type-II</td>
<td>H2: 52.44</td>
<td>2.45</td>
<td>Re:0.80</td>
<td>[149]</td>
</tr>
<tr>
<td>WO3@g-C3N4</td>
<td>self-assembly</td>
<td>Area-area contact</td>
<td>S-scheme</td>
<td>H2: 49.1</td>
<td>1.84</td>
<td>Re:0.61</td>
<td>[46]</td>
</tr>
<tr>
<td>CdS@g-C3N4</td>
<td>in situ hydrothermal growth</td>
<td>Area-area contact</td>
<td>S-scheme</td>
<td>H2: 76.5</td>
<td>1.72</td>
<td>Re:1.65</td>
<td>[150]</td>
</tr>
<tr>
<td>Co3(PO4)2@g-C3N4</td>
<td>direct precipitation</td>
<td>Area-area contact</td>
<td>Type-II</td>
<td>H2: 18.78, O2: 8.87</td>
<td>Re:0.550O:0.11</td>
<td>Re:1.220O:1.65</td>
<td>[151]</td>
</tr>
<tr>
<td>MnOx@g-C3N4/GdS/Pt</td>
<td>chemical-annealing photoreduction</td>
<td>Area-area contact</td>
<td>Type-II</td>
<td>H2: 61.34 O2: 30.33</td>
<td>Re:0.46O:0.11</td>
<td>Re:0.66O:1.63</td>
<td>[152]</td>
</tr>
<tr>
<td>RuO2/α-Fe2O3@g-C3N4</td>
<td>heated</td>
<td>Area-area contact</td>
<td>Z-scheme</td>
<td>H2: 0.38 O2: 0.19</td>
<td>Re:1.36</td>
<td>Re:1.21O:2.43</td>
<td>[135]</td>
</tr>
<tr>
<td>g-C3N4/rGO/PDIP</td>
<td>wet-chemistry reduction and solvent</td>
<td>Area-area contact</td>
<td>Z-scheme</td>
<td>H2: 15.80 O2: 7.80</td>
<td>Re:1.64</td>
<td>Re:0.93O:0.87</td>
<td>[133]</td>
</tr>
<tr>
<td>WO3H2O/g-C3N4</td>
<td>hydrothermal</td>
<td>Area-area contact</td>
<td>Z-scheme</td>
<td>H2: 48.2 O2: 23.2</td>
<td>Re:0.89</td>
<td>Re:1.01O:3.13</td>
<td>[153]</td>
</tr>
</tbody>
</table>

Fig. 13. The possible pathways of photocatalytic CO2 reduction to C1 and C2 products, where a denotes reduction potential (vs. SHE, pH=7) and b for electrons required during the reactions.
5.2. Photocatalytic CO₂ reduction

CO₂ is thermodynamically stable and requires high dissociation energy (~750 kJ/mol) to break the C=O bond during the conversion process [154]. Alternatively, light-driven CO₂ reduction is effective to overcome the thermodynamic barrier attributing to the energetic hot carriers [155]. Considering insufficient utilization of the clean, and widely distributed solar energy [156], practical application of light-driven CO₂ conversion is an ideal way to attenuate CO₂ concentration and produce high value-added chemicals simultaneously.

Photocatalytic CO₂ reduction reactions mainly includes three steps (taking H₂O as a hole capture agent): (1) Absorption of photons with suitable energy followed by excitation of electron-hole pairs; (2) Separation and migration of electrons and holes to suitable redox reaction sites; (3) Occurrence of a redox reaction at the surface, so that electrons reduce CO₂ to C₁ and C₂ + chemicals such as CO, CH₄, CH₂OH, C₂H₆, while holes oxidize H₂O to O₂. Photocatalytic reduction of CO₂ to hydrocarbon fuels is an uphill reaction with a substantially high Gibbs free energy, thus abundant energy is desired to overcome the reaction barriers and facilitate the overall photocatalytic efficiency.

Fig. 13 summarizes the pathway of photocatalytic CO₂ conversion to various products based on different reduction potentials and electron transfers [157]. For instance, 2 electrons are required for the formation of CO (~0.51 V vs SHE), while 14 electrons account for the formation of C₂H₆ (~0.27 V vs SHE). Since CO₂ reduction is a complex multi-electron transfer process, it needs suitable electrons for the generation of different products on the react interface [158]. Therefore, the influence of interfacial engineering on the accumulation of hot electrons and selectivity in the photocatalytic reduction of CO₂ is worth to be discussed.

Transitional metal oxides such as TiO₂ are frequently utilized to hybridize with g-C₃N₄ as photocatalysts in reducing CO₂ to obtain C₁ products [159]. The TiO₂/g-C₃N₄ composites reported by Shi et al. have demonstrated a high selectivity of CO₂ reduction to CO [160]. However, different selectivity preference towards CH₄ rather than CO was found in a TiO₂/MoS₂/g-C₃N₄ system fabricated by Kang et al. [161]. To figure out the mechanism, Wang et al. used first-principle calculation to demonstrate the free energy profiles of CO₂ conversion on g-C₃N₄/TiO₂ (Fig. 14a) [162]. It is concluded that the product of CO₂ reduction is dependent on the adsorption and desorption energy of intermediate products on the surface of the photocatalyst. The addition of MoS₂ can effectively reduce the reaction energy for methane. Meanwhile, a giant IEF after MoS₂ addition was formed, which would induce more energetic hot electrons at the interface for a high methane selectivity.

Fig. 14. (a) The calculated free energy profile of g-C₃N₄/TiO₂. Reproduced with permission [162]. Copyright 2021, Royal Society of Chemistry. (b) The CO₂ conversion intermediates with BTN and BTN-CNDs from in-situ DRIFT spectra. Reproduced with permission [163]. Copyright 2017, Elsevier. (c) Proposed mechanism for electron transfer of OCAL. Reproduced with permission [164]. Copyright 2018, Elsevier. (d) The schematic mechanism of BPA removal over model I for Bi₂S₃/g-C₃N₄ (BS/GCN) and model II over functional group modified Bi₂S₃/g-C₃N₄ (FGBS/GCN) under simulated irradiation. Reproduced with permission [57]. Copyright 2018, Wiley-VCH.
separation, while larger BPD provides rich electronic environment for multi-electron CO₂ photoreduction, which is more inclined to generate valuable hydrocarbon products. As for the in-plane heterostructure, the selectivity of value-added products can still be high when the IPD is relatively low even if the IPD driving force exists along the lateral direction in the intraplane heterostructure. IEF maximizes the utilization of active electrons and holes to orderly participate in reduction process. For an inter-plane system, the generation of products such as CH₄ and CH₃OH requires a higher IPD to ensure the abundance of electrons. But for an in-plane heterojunction, BPD seems to play a more important role than IPD. It can be seen from Table 2 that high reduction rates are often obtained on in-plane heterojunctions with high BPD. Therefore, IPD may be more vital in the inter-plane heterostructures including Type-II and S-scheme heterojunctions. For the in-plane IEF systems, controlling BPD can be a promising way for improving and regulating CO₂ selectivity.

Based on the abovementioned discussions, the IEF effect on the selectivity of photocatalytic CO₂ reduction can be concluded into the following five main aspects. (1) The selectivity of products is largely relied on reactant adsorption energy, while interfacial engineering could change the energy barrier between the reactants and photocatalysts. For instance, metal or metal-like co-catalysts coupled with g-C₃N₄ heterojunctions can serve as both active sites and electron-rich region for CO₂ reduction. This could be attributed to the different adsorption energies caused by the interaction between v-band of metals and the orbitals of adsorbent molecules. Furthermore, g-C₃N₄ is mainly used as an adsorption and activation site, providing a solid land for adsorption and sequential reaction of CO₂. (2) Owing to the difference in the work functions of the components in a heterojunction, the electrons move directly from the component with low work function to the component with high work function to achieve the equilibrium of Fermi level. Thus, defective energy levels stemmed from various photocatalysts are introduced to form different heterojunction pathways and interfacial IEF is formed to pose driving forces on photo-induced charge carriers. (3) The intimate contact of the dual or ternary photocatalysts exhibits promising IEF, which poses interfacial electric field force on charge carriers to drive them separation and accumulation at the interface. The more energetic hot carriers at the interface would provide room for multiple-electron reduction of CO₂ with a higher activity and satisfied selectivity of target products. Meanwhile, the constructed heterostructure with interfacial IEF also benefited reliable resistance against photocorrosion for promoted stability and durability. (4) Interfacial regulations not only exert effects on the free energy of intermediate products in the process of CO₂ conversion, but also can intensify the IEF for an active region enriched with more energetic hot carriers. (5) Both IPD and BPD values of the as-formed heterojunctions can be modulated by interfacial engineering. IPD dominates the photo-excited charge dynamics at the interface while BPD determines the productivity and selectivity in photocatalytic CO₂ reduction.

### 5.3. Photocatalytic degradation of pollutants

Advanced oxidation processes (AOPs) are fascinating pathways to remove the anthropic health threats of persistent organic pollutants (POPs) in water. However, AOPs such as photo-Fenton, Fenton-based processes and persulfate (PMS) activation are facing an intractable problem to produce reactive species for oxidation of POPs in water [176, 177]. Alternatively, photocatalysis as one of the most promising strategies of AOPs has drawn intensive attention in degradation and mineralization of POPs owing to its clean, sustainable and stable advantages [178–180].

In a photocatalytic degradation process, photo-generated holes/electrons with strong oxidizing/reducing potentials are involved into the generation of specific ROS at the active sites of catalyst surface [181, 182], thus the recombination rate of photoinduced charge carriers should be restrained. Moreover, the redox ability determined by the potentials of VB and CB is another crucial factor to influence the

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### Table 2: Photocatalytic CO₂ reduction over g-C₃N₄-based photocatalysts for IEF design.

<table>
<thead>
<tr>
<th>photocatalysts</th>
<th>Synthesis method</th>
<th>Interfacial effect</th>
<th>Type of Heterojunction</th>
<th>Activity Rate/μmol h⁻¹</th>
<th>IPD (eV)</th>
<th>BPD (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsPbIₓBrᵧ</td>
<td>hydrothermal</td>
<td>Point-area contact</td>
<td>Type II</td>
<td>CO: 1.19</td>
<td>0.28</td>
<td>0.07 (CO)</td>
<td>[165]</td>
</tr>
<tr>
<td>CdsPbIₓBrᵧ</td>
<td>solution mixing</td>
<td>Point-area contact</td>
<td>type II</td>
<td>CO: 0.01</td>
<td>1.08</td>
<td>0.22 (CO)</td>
<td>[166]</td>
</tr>
<tr>
<td>SnSₓ</td>
<td>in-situ assembly</td>
<td>Point-area contact</td>
<td>Z scheme</td>
<td>ChCl: 0.03</td>
<td>2.01</td>
<td>0.78 (ChCl)</td>
<td>[167]</td>
</tr>
<tr>
<td>TiO₂-C₃N₄</td>
<td>thermal condensation and electrostatically assembly</td>
<td>Area-point-area contact</td>
<td>S-scheme</td>
<td>ChCl: 0.13</td>
<td>2.30 (TiO₂ to g-C₃N₄)</td>
<td>0.93 (CO)</td>
<td>[168]</td>
</tr>
<tr>
<td>SnSₓ/g-C₃N₄</td>
<td>one-step in situ hydrothermal</td>
<td>Point-area contact</td>
<td>S-scheme</td>
<td>CH₄0.032</td>
<td>1.84</td>
<td>1.14 (CH₄OH)</td>
<td>[169]</td>
</tr>
<tr>
<td>Bi₂Se₃</td>
<td>molten-salt assisted method and CVD</td>
<td>In-plane contact</td>
<td>In-plane type II</td>
<td>CO: 0.08</td>
<td>0.02</td>
<td>0.22 (CO)</td>
<td>[170]</td>
</tr>
<tr>
<td>NS-g-C₃N₄</td>
<td>NH₃-mediated</td>
<td>In-plane contact</td>
<td>In-plane</td>
<td>ChCl: 0.14</td>
<td>0.08</td>
<td>0.84 (CH₄OH)</td>
<td>[171]</td>
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<tr>
<td>p-C₃N₄ @Hm-C</td>
<td>thermal polymerization</td>
<td>In-plane contact</td>
<td>In-plane</td>
<td>CO: 1.65</td>
<td>0.65</td>
<td>0.66 (CH₄)</td>
<td>[172]</td>
</tr>
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<td>Bi₂Se₃@g-C₃N₄</td>
<td>mixing</td>
<td>Area-point contact</td>
<td>type II</td>
<td>CO: 0.41</td>
<td>0.80</td>
<td>0.57 (CO)</td>
<td>[173]</td>
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<td>ZnV₂O₆/</td>
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<td>Area-point contact</td>
<td>type II</td>
<td>CO: 32.37</td>
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<td>0.40 (Ch₃OH)</td>
<td>[174]</td>
</tr>
<tr>
<td>g-C₃N₄</td>
<td>thioacetamide</td>
<td>Line-area contact</td>
<td>S-scheme</td>
<td>ChCl: 37.42</td>
<td>2.44 (TiO₂ to g-C₃N₄)</td>
<td>0.34 (CO)</td>
<td>[161]</td>
</tr>
<tr>
<td>Au/Au-TiO₂</td>
<td>self-assembly by hydroxyl condensation</td>
<td>Area-area contact</td>
<td>Z-scheme</td>
<td>CH₃: 0.09</td>
<td>1.06 (Ch₄)</td>
<td>0.71 (Ch₄)</td>
<td>[175]</td>
</tr>
<tr>
<td>Ti₃C²₋/g-C₃N₄</td>
<td>direct calcination</td>
<td>Area-area contact</td>
<td>Schottky heterojunction</td>
<td>Ch₃: 0.10</td>
<td>0.31</td>
<td>0.42 (CO)</td>
<td>[61]</td>
</tr>
</tbody>
</table>

---
photocatalytic degradation efficiency of POPs [183,184]. Recently, g-C₃N₄ as a promising and tunable conjugated polymer semiconductor with merits of metal-free, low-cost and visible light-response has been explored in the fields of not only solar energy conversion but also environmental remediation and resource recycling [185–187]. Therefore, interfacial engineering for regulating the dynamics of charge carriers and steering the activity of free radical and nonradical ROS could be achieved and well worth discussing.

Nevertheless, it is acknowledged that the weak driving force of pristine carbon nitride on photo-excited charge carriers impedes the charge dynamics and degradation rates. Therefore, fabrication of heterojunction with interfacial engineering for regulating the charge dynamics and steering the activity of free radical and nonradical ROS is required.

Carbon nitride is a perfect support to host other components. As such, the symmetric structure of carbon nitride can be easily broken by heterojunction fabrication to tackle the problem of low-carrier-EROjunction. Such, the symmetric structure of carbon nitride can be easily broken by heterojunction fabrication to tackle the problem of low-carrier-efficiency. Wu et al. reported a Z-scheme heterojunction of oxygen-doped g-C₃N₄ (OCN)/CoAl-layered double hydroxide (OCAL) for degradation of methyl orange (MO) [164]. The MO removal rate elevates with the increasing of OCN content. The introduction of Co²⁺ and Al³⁺ into OCN could generate additional exposed sites and build IEF at the interface to promote higher separation and diffusion efficiency of charge carriers. The charge diffusion pathway follows the typical Z-scheme mechanism in the heterojunction (Fig. 14c). The holes with strong oxidation ability at the VB of the OCN oxidize OH to •OH while the electrons at the CB of the CoAl-LDH are able to activate oxygen to O₂. This transfer process is also confirmed by DFT theoretical calculations. The difference in work functions and flat band potentials between OCN and OCAL promote the electron flow to achieve the equilibrium of Fermi levels, thus building the intrinsic electric field (IEF) in OCN/OCAL heterojunction. Bader charge analysis proves that the IEF is created by the difference in work functions and flat band potentials between OCN and OCAL heterojunction (Fig. 14d). The electrons accumulated on the CB of the Bi₂S₃ (BS) are not reductive enough to generate •O₂ radical. The holes on BS/GCN are the main active species in photocatalytic BPA degradation. While in FGBS, the CB position is more negative than that of BS and conducive to the formation of •O₂ radicals, which become the dominant ROS in the BPA degradation. A wider spatial charge region with a giant IEF after the subsequent participation in ROS generation. Hence, it can be concluded that the FGBS/GCN p-n heterojunction strengthens the IEF by regulating the charges migration pathway and optimizes the band structure to make the generation of •O₂ viable, resulting in the highest BPA

<table>
<thead>
<tr>
<th>g-C₃N₄-based photocatalysts (pollutant)</th>
<th>Synthesis method</th>
<th>Interfacial effect</th>
<th>Type of heterojunction (Dominant ROS)</th>
<th>Catalytic efficiency</th>
<th>Kobs (min⁻¹)</th>
<th>IPD (eV)</th>
<th>BPD (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dots/g-C₃N₄ (SDZ)</td>
<td>pyrolysis</td>
<td>Point-area contact</td>
<td>(•O₂ and h⁺ coupling, nonradical dominant)</td>
<td>92.8% (80)</td>
<td>0.0320</td>
<td>0.08</td>
<td>1.21</td>
<td>[93]</td>
</tr>
<tr>
<td>Carbon sphere/g-C₃N₄ (SCP)</td>
<td>hydrothermal via surfactants</td>
<td>Point-area contact</td>
<td>(radical •O₂)</td>
<td>100% (180)</td>
<td>0.0381</td>
<td>1.00</td>
<td>0.95</td>
<td>[67]</td>
</tr>
<tr>
<td>CdS/g-C₃N₄ (RhB)</td>
<td>two-step self-assembly</td>
<td>Line-area contact</td>
<td>Type-II (•O₂ and h⁺ coupling)</td>
<td>95% (150)</td>
<td>0.0701</td>
<td>Rx: 0.66</td>
<td>0.22(•O₂)</td>
<td>[188]</td>
</tr>
<tr>
<td>α-Fe₂O₃/g-C₃N₄ (nitrile oxide)</td>
<td>hydrothermal method</td>
<td>Area-area contact</td>
<td>Z-scheme (•O₂ and •OH)</td>
<td>60.8% (30)</td>
<td>-</td>
<td>1.08</td>
<td>1.16(•O₂)</td>
<td>[80]</td>
</tr>
<tr>
<td>O-doped g-C₃N₄/CoAl-LDH (MO)</td>
<td>in-situ hydrothermal growth</td>
<td>Area-area contact</td>
<td>Z-scheme (•O₂ and •OH)</td>
<td>99.7% (60)</td>
<td>0.0960</td>
<td>40.3%</td>
<td>0.97</td>
<td>[164]</td>
</tr>
<tr>
<td>Mn₂O₃/C@g-C₃N₄ (TC)</td>
<td>electrostatic self-assembly</td>
<td>Area-area contact</td>
<td>VDW (•O₂ and h⁺ coupling, nonradical dominant)</td>
<td>97% (60)</td>
<td>0.0660</td>
<td>76% (120)</td>
<td>0.60</td>
<td>[189]</td>
</tr>
<tr>
<td>BiVO₄/g-C₃N₄ (RhB)</td>
<td>electronic self-assembly</td>
<td>Area-area contact</td>
<td>S-scheme (•O₂ and •OH)</td>
<td>93% (40)</td>
<td>0.0428</td>
<td>1.62</td>
<td>0.37(•O₂)</td>
<td>[190]</td>
</tr>
<tr>
<td>g-C₃N₄(thioarene)/g-C₃N₄(area) (MO)</td>
<td>protonation-assisted hydrothermal</td>
<td>Area-area contact</td>
<td>Type-II (•O₂ and h⁺ coupling)</td>
<td>97% (180)</td>
<td>0.0233</td>
<td>Rx: 0.22</td>
<td>0.15(•O₂)</td>
<td>[191]</td>
</tr>
<tr>
<td>TiO₂/high-crystalline g-C₃N₄ (TC)</td>
<td>hydrothermal</td>
<td>Area-area contact</td>
<td>Type-II (•O₂ and •OH coupling)</td>
<td>90% (120)</td>
<td>0.0203</td>
<td>Rx: 0.77</td>
<td>0.24(•O₂)</td>
<td>[192]</td>
</tr>
<tr>
<td>Cu₂O/g-C₃N₄ (MO)</td>
<td>hydrothermal reduction with acid exfoliation</td>
<td>Area-area contact</td>
<td>Type-II (•O₂ and h⁺ coupling)</td>
<td>84% (30)</td>
<td>0.0680</td>
<td>Rx: 1.13</td>
<td>1.33(•O₂)</td>
<td>[193]</td>
</tr>
<tr>
<td>FGBS/g-C₃N₄ (BPA)</td>
<td>hydrothermal</td>
<td>Area-3D cavity contact</td>
<td>p-n (radical •O₂)</td>
<td>−70% (240)</td>
<td>0.0045</td>
<td>1.36</td>
<td>0.37(•O₂)</td>
<td>[57]</td>
</tr>
<tr>
<td>BiOBr/P-doped g-C₃N₄ (AB 28)</td>
<td>hydrothermal polymerization</td>
<td>Area-3D contact</td>
<td>S-scheme (h⁺, •OH and •O₂, nonradical dominant)</td>
<td>99.99% (80)</td>
<td>0.0333</td>
<td>1.75</td>
<td>0.31(•O₂)</td>
<td>[49]</td>
</tr>
</tbody>
</table>
degradation rate constant.

Table 3 summarizes the type of charge transfer and contact in reported g-C3N4-based heterojunction, the main ROS as well as BPD/IPD values in photocatalytic degradation processes. IPD and BPD values are both higher in radical-dominant degradation processes than that controlled by non-radical reactions, which will lead to higher oxidation abilities. Generally, IPD is responsible for accelerating the dynamics of photo-excited charge carriers at the interface. As such, an enlarged IPD always leads to a higher degradation rate of contaminants. \( \text{O}_2 \) is accompanied in most photocatalytic degradation processes as oxygen can be easily activated by the photo-excited hot electrons. For generation of OH, the band energy levels should be more positive/negative with high oxidative/reductive potentials to achieve a high BPD. Considering the high BPD in Z-/S-scheme heterojunctions, radical species (\( \bullet \text{O}_2 \)) are easily detected in some Type-II heterostructures. However, the hydroxyl radicals are not generated via oxidation at the VB of the photocatalyst, but via the \( \text{H}_2\text{O}_2 \) reduction generated by the \( \text{O}_2 \) at the CB. Therefore, constructing heterojunctions with high IPD and BPD could be favorable to realizing a high degradation rate with a radical-dominant degradation pathway.

In conclusion, photocatalytic degradation of environmental pollutants can be ascribed to interfacial engineering of the IEF in three aspects. (1) IEF promotes charge dynamics and regulates charge migration pathways, enabling more energetic photo-generated holes/electrons to activate more reactive ROS with larger quantity at the high oxidation/reduction potentials. (2) The strong coupling of IEF and large intimate contact (point, line and surface contact) and laterally expand the conduction channel on charge carriers will eventually result in intensified charge dynamics. It should be mentioned that 2D/2D heterojunction provides the largest separation channels for charge carriers and intralayer heterojunction exhibits the shortest diffusion pathway for hot carriers. As thus, these two kinds of heterojunctions are the promising heterostructures for dynamic enhancement of charge carriers. (iii) The configuration IEF on hot carriers also remarkably promotes their outputs for redox reaction, realizing higher reaction rates in various photocatalytic processes. Besides, IEF engineering can improve reaction selectivity by changing the transferring pathway of hot carriers. The energized hot carriers will selectively participate into redox reactions for a high yield of targeted products. In addition, the photocorrosion resistance and reusable of the developed photocatalysts remain after various IEF modulations.

Currently, considerable enthusiasm has been aroused on interfacial engineering in different types of heterojunctions to fabricate and modulate IEF. Although a significant progress on the enhanced charge dynamics and photocatalytic throughputs has been achieved, the state-of-the-art heterojunction is still far from practical application. From the aspect of catalysts, the interface of most heterojunctions is still limited so that the IEF is under-powered for an unsatisfactory photocatalytic process. In addition, the long diffusion path of charge carriers after separation at the interface easily leads to their decay in the form of heat, rather than participation into the redox reaction. From the aspect of mechanism, the structure-performance relationship in the emerging heterojunction is rarely studied. Additionally, unveiling the relationship between IEF and ROS in a photooxygenation process will selectively acquire the targeted active species for the products to achieve oriented design and development of heterojunctions. Based on this, efforts devoted to the following aspects are hopeful to promote the development of IEF mediated photocatalysis.

(I) For IEF design, S-scheme heterojunction includes the merits of other types of heterojunction, such as promoted charge dynamics and robust redox capabilities. Meanwhile, fast dynamics and long lifetime of charge carriers are realized in carbon nitride intralayer heterojunction. As such, developing more carbon nitride-based S-scheme in-plane heterojunction is expected to achieve a high photocatalytic apparent quantum efficiency. In addition, a single atom catalyst with unique coordination environment has exhibited a superb pumping effect on charge carriers, which dramatically drives charge carrier’s separation and accumulation on the specific regions. Therefore, more carbon nitride based single atom photocatalysts with a strong localized IEF are highly desirable.

(II) For IEF fabrication, the IEF built by a top-down strategy, such as epitaxial growth, is more uniform and repeatable than the widely used bottom-up approaches. As such, more top-down approaches are anticipated to be explored. Additionally, the direction of IEF plays an equal importance with IEF intensity on the photocatalytic performance. Specifically, the direction of IEF to the active sites would enable hot carriers to participate into a redox reaction in the shortest time. Conversely, in spite of a fast separation rate, more hot carriers would decay in the form of heat once the direction of IEF deviates from the active sites, leading to a lower photocatalytic performance. Therefore, revealing the effect of IEF direction on photocatalytic performance and fabrication of specific directional IEF towards active sites are of the vital importance.

(III) For IEF modulation, the structure-performance relationship of heterojunction is to be unveiled imminently. In detail, identification of active sites on heterojunction is beneficial to guide IEF controlling. Taking Pt nanoparticle loaded carbon nitride as an example, two remarkably enhanced electric fields locate at the Pt-
C$_2$N$_4$ interface and Pt surface under light irradiation. Therefore, it is necessary to distinguish the active region in photocatalysis, so that it can be targeted to regulate IEF at the active region for enhanced photocatalysis.

(IV) For IEF monitoring, quantitative analysis of IEF in the fabricated heterojunctions is also critical. It is urgent to develop more detailed characterization techniques, especially in situ irradiation techniques to directly observe or quantitatively detect IEF in heterojunctions. In addition, simulation methods can be employed to predict the IEF intensity before the IEF fabrication, rendering IEF engineering more efficient.

(V) For IEF applications, further broadening the scope of IEF application is a critical task towards practical energy conversion processes, such as organic synthesis and CI chemistry. Meanwhile, the environmental compatibility and catalytic stability of heterojunctions are particularly inspected. Besides, IEF regulation for selective synthesis of high-value-added chemicals in CO$_2$ reduction and selective activation of active oxygen species in photocatalysis or photocatalytic degradation processes is another orientation in IEF-driven photocatalysis. Also, it is necessary to maximize the utilization of reactive sites on heterojunction to promote a grand scale use in the future. It is expected that more promising carbon nitride-based heterojunctions equipped with giant IEF are developed into photocatalytic devices for highly efficient light harvesting and energy conversion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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