Internal electric field engineering for steering photogenerated charge separation and enhancing photoactivity

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Abstract
Photocatalysis as a desirable technology shows great potential in environmental remediation and renewable energy generation, but the recombination of photogenerated carriers is a key limiting factor for efficiency in artificial photosynthesis. Internal electric field (IEF, also known as built-in electric field) engineering acts an emerging and clearly viable route to increase photocatalytic efficiency by facilitating charge separation and transfer. This review summarizes the basic principles of IEF including the source, the strategies for the enhancement and the measurement of IEF. Highlight is the recent progress in steering photogenerated charge separation of photocatalysts by IEF engineering and related mechanisms. Finally, the challenges in IEF engineering and exciting opportunities to further enhancing charge separation and photocatalytic performance are discussed.

KEYWORDS
built-in electric field, internal electric field, photocatalysis, photogenerated charge separation

1 | INTRODUCTION
Energy shortages and environmental pollution problems seriously pose a serious threat to the sustainable development of society. Therefore, there is an urgent need to develop environmentally friendly and renewable technologies for green energy production and environmental restoration. Semiconductor photocatalysis has been considered as a highly desirable and green strategy to solve the aforementioned issue because it directly utilizes solar energy with unparalleled resource potential both for the production of valuable chemical fuels, such as hydrogen and hydrocarbon fuels, and for the degradation of harmful contaminants.1-5

One of the key limiting factors affecting efficiency in artificial photosynthesis is the recombination of photogenerated carriers. After excitation from incoming photons of suitably high energy, electron-hole (e−-h+) pairs are formed in photocatalyst during a few femtoseconds; then the e− or h+ migrate across both the bulk and the surface of photocatalyst to arrive at the catalytically reactive sites on the picosecond timescale, where the surviving electrons and holes catalyze water splitting, CO2 reduction, and contaminant degradation on a time scale of a several nanoseconds to a several microseconds.4,6 Thus, it is imperative to explore strategies in order to make e−-h+ pairs separated as far as possible on the photocatalyst. In this respect, substantial work has been devoted to explore and design novel photocatalytic systems benefiting charge separation and the improvement of the photocatalytic efficiency.7 Several strategies, including heterojunctions,8-10 phase junctions,11,12...
crystal-facet engineering,13 cocatalyst loading,14,15 and doping16 have been developed and made substantial contributions to highly efficient charge separation and high performance of photocatalytic systems. Despite these efforts, advances on charge separation steering receive limited success, and new strategies are required to promote photogenerated charge separation.17,18

As everyone knows that electric fields promote the directed migration of charges. Based on this theory, an external electric field is applied to a photocatalyst fixed in the form of an electrode to promote the directional migration of photogenerated charges and the separation of $e^- - h^+$ pairs, which is defined as photoelectrocatalysis. Unfortunately, the external voltage cannot be applied to non-fixed photocatalysts, in particular it also brings about a bit of additional energy consumption, which limits its driving effect on the photocatalytic process. Naturally, we divert attention to the use of self-built electric fields that are not limited by the form of photocatalyst and without additional energy consumption, which is caused by dipoles inside the photocatalyst to promote carrier separation.19,20 Recently, internal electric field (IEF) engineering has emerged as an efficient method to improve photogenerated charge separation both in bulk and on the surface of photocatalysts.21-28 However, at present, there is not only a lack of deep understanding of the IEF, but also a review on the applications of IEF in the field of photocatalysis. In addition, a systematic description of the testing methods and enhancement strategies of IEF has not been reported.

In this review, we focus on using IEF engineering to promote the migration of photogenerated charge in photocatalytic processes. Firstly, we describe the basic principles of IEF including the source, the strategies for the enhancement and the measurement of IEF. Secondly, we present the mechanism of IEF promoting photoactivity and various photocatalytic applications of IEF to provide a well-organized overview and better understand the IEF engineering for steering photogenerated charge separation. Finally, we give the prospects of the future development of IEF in photocatalysis.

2 | SOURCE OF IEF

2.1 | Intrinsic IEF

The chemical units that make up the unit cell have different electronegativity, and their ordered arrangement produces dipole moments. Components that exhibit positive and negative centers must not overlap in order to produce local IEF, which means that local IEF is closely related to the structure of unit cell.23-28 For example, bismuth semiconductors may form an anisotropic layered structure in which the positive and negative layers are arranged in an ordered manner, as shown in Figure 1A, creating dipoles between the layers,23-26,28 thereby producing IEF. In addition, IEF is also constitutes between different crystal faces of the unit cell, mainly because various atomic structures of crystal faces results distinct potentials, which generate IEF inside the unit cell (Figure 1B). For organic compounds, permanent dipoles are created due to electron transfer phenomena of different groups in polar molecules,29,30 thus forming the IEF of the molecule.

2.2 | Induced IEF

In the case where the photocatalyst does not have intrinsic local IEF, the charge distribution can be changed by
various external environments to generate an induced dipole (Figure 1C). For example, uneven doping of the photocatalyst causes electron cloud to deform and the positive and negative electric centers to be noncoincident, thereby generating electron absorption and electron donating centers.\textsuperscript{31-33} Due to the difference in work function of different semiconductor materials combined into a composite, electrons are migrated from one semiconductor to another, thus forming IEF at the interface that becomes a driving force for photogenerated carrier migration.\textsuperscript{34,35} The charge distribution of the photocatalyst changes when some polar molecules are closed to photocatalyst, and induce the surface electric field resulting the ordering migration of photogenerated charge.\textsuperscript{36-38} For polarized semiconductors such as dielectric, ferroelectric, and piezoelectric, the induced dipole is generated by the polarization phenomenon of applied electric field, pressure, and so forth, thus promoting the separation of photogenerated charges.\textsuperscript{39}

### 3 | STRATEGIES FOR THE ENHANCEMENT OF IEF

The essence of IEF enhancement is to enhance the uneven distribution of charge in photocatalyst. According to the current literature, we summarize the following five strategies to change the charge distribution and induce the generation of dipole to enhance the IEF.

1. **Changing the unit cell structure to enhance the IEF.**
   As mentioned earlier, IEF is caused by the dipole inside the unit cell, and the structure of unit cell changes as well as adjusting the positive and negative electric centers, thus enhancing the local IEF.\textsuperscript{21,40}

2. **Adjusting the structure of organic compounds by adding groups to enhance the IEF.**
   The electronegativity of substituents has a significant effect on the electronic distribution and molecular dipole of organic molecular photocatalysts. According to the electronic cloud of the modified photocatalyst, the molecular dipole and the IEF can be effectively increased by choosing appropriate substituents.\textsuperscript{29,30,41}

3. **Doping high electronegative elements to enhance the IEF.**
   The IEF depends on the charge distribution of the material that is closely related to the photocatalyst’s chemical composition. By doping the elements with different electronegativity from the original photocatalyst, the electron absorption effect changes the distribution of the original electron cloud, which eventually leads to the enhancement of IEF.\textsuperscript{31-33,42}

4. **Interfacial interaction to enhance the IEF.**
   Choosing semiconductors with large work function difference or small difference but large interface contact area to prepare composite photocatalysts, both can achieve the goal of enhancing the interface effect and enhancing the IEF.\textsuperscript{43-45}

5. **Induced polarization semiconductor materials to enhance the IEF.**
   Dielectric, ferroelectric, piezoelectric, and other polarized semiconductors can polarize or produce macro-polarization internally under suitable external electric field, pressure, temperature, and other conditions, as a result improving the IEF.\textsuperscript{39,46}

### 4 | MEASUREMENT OF IEF

Quantifying the IEF is necessary to study its effect on photocatalytic activity. On the one hand, the theoretical value of IEF can be measured by density functional theory (DFT). On the other hand, the experimental values of the IEF can be measured by macroscopic characterization. Combined with the results of theory and experiment, a deterministic assessment of the trend of IEF can be performed.

#### 4.1 | Theoretical calculation

For inorganic compounds of the periodic system, it is integrated along the desired direction of unit cell according to the electrostatic potential calculated by DFT, and the electrostatic potential difference is the expression for IEF strength of the unit cell. Li et al. calculated the electrostatic potential differences ($\Delta E$) between [Bi$_2$O$_4$] and [Cl] slices by this DFT method, (Figure 2A), indicating that $\Delta E$ of C doping is as high as 7.36 eV, which is 2.1 times that of undoped. The size of $\Delta E$ represents the intensity of local IEF of the unit cell, which indicated doping intensified the nonuniform distribution of charge between the layers to the most extent might, meaning that C doping might be an efficient strategy to boost the IEF of Bi$_3$O$_4$Cl.\textsuperscript{23} Through the similar calculation method, our group recently calculated the local electrostatic potential differences ($\Delta U$) to obtain the local IEF of BiO$_x$, Bi$_4$O$_{10}$I$_2$, and Bi$_5$O$_{11}$Cl$_2$.\textsuperscript{47} Firstly, the [-Bi-O-], [-Bi-Bi-], and [-I-I-] part are divided along the layered stacking direction of bismuth oxyiodide crystal cell. The computational results stating in Figure 2B imply that the difference of local electrostatic potential is small in [-O-Bi-] and [-Bi-I-], but large in [-I-I-]. Bi$_5$O$_{11}$I with the lowest I content represents an electrostatic potential of 28.22 eV, which is attributed to the influence of O on the IEF of [-I-I-] to varying degrees due to the decrease in I. The DFT results preliminarily revealed that the reduction of I induces the enhancement of IEF. The electrostatic potential difference is a currently accepted and
widely used method for calculating the local IEF of an inorganic photocatalyst, but since there is no sophisticated procedure for calculating the local dipole moment of a unit cell, there is little data for intuitively reacting the dipole moment. 

For organic compounds with a nonperiodic system, the dipole moment calculated by DFT can visually represent the local electric fields of the photocatalyst, and the direction can be determined according to the electron density. Weingarten et al. synthesized a series of chromophore amphiphiles (CAs). An electron-donating amine (NH₂-CA), electron-neutral methyl (CH₃-CA) or electron-withdrawing nitrile (CN-CA) was attached to the nine-position of perylene monoimide's (PMI) aromatic core, which usually affect the core's electronic properties, such as band gap, HOMO-LUMO levels, and dipole strength. They used the B3LYP/6–311++G(d,p) hybrid function and basis set to calculated dipole moments for PMI, NH₂-CA, CH₃-CA, and CN-CA to be 7.1, 10.2, 8.1, and 1.6 D, respectively (Figure 2C). The dipole moment calculated by DFT intuitively reflects the change of the molecular dipole. NH₂-CA’s strong molecular dipole is consistent with π-donation by the amine nitrogen’s lone pair, while CN-CA’s weak dipole results from competition for electron density between the electron-withdrawing nitrile and imide groups. CH₃-CA’s weakly donating methyl group enhances the core dipole relative to unsubstituted PMI. Based on the DFT result that showed a decreasing trend in molecular dipole strength as the nine-position’s electron-withdrawing nature is increased, they demonstrated that substituent choice control the dipole strength of organic molecule that. 

For composites, it is first necessary to determine the crystal planes that make up the interface according to the electrostatic potential diagrams of X (X = P, S, N, B, F, Br, and C) doped Bi₃O₄Cl. DFT calculated local internal electric field ΔU for bismuth oxyiodide with different crystal structures. The purple, gray and red shaded parts represent the local electric fields of [-Bi-I-], [-I-I-] and [-Bi-O-], respectively; DFT, density functional theory.
electron micrograph, then calculate the work function of these crystal faces by DFT. When two materials with differing Fermi levels are brought into contact, there will be a discontinuity in the Fermi level at the interface. This progress will cause electron transfer from the material with a higher Fermi level to a lower Fermi level to establish an equilibrium. As a result, a potential difference called the contact potential difference (CPD) as well as a build-up of a dipole layer at the interface is formed between the two materials.\(^3\)\(^4\) Therefore, the difference in work function is the CPD of the complex, which forms the IEF of the interface.\(^3\)\(^4\) The surface work functions of the monolayers g-C\(_3\)N\(_4\) (001) and TiO\(_2\) (100) were 5.22 eV and 6.43 eV, respectively. When they combine to form a Z-type heterojunction, electrons transfer from the single layer g-C\(_3\)N\(_4\) with a lower work function to TiO\(_2\) with a higher work function until equilibrium is reached, resulting in the formation of IEF from g-C\(_3\)N\(_4\) (001) to TiO\(_2\) (100) at the interface (Figure 2D), which extends the lifetime of the photogenerated carriers.\(^5\)\(^0\)

### 4.2 Experimental measurement

#### 4.2.1 IEF measurement of a single photocatalyst

In addition to theoretical calculations, the experimental values of the IEF can be measured by macroscopic characterization. In the case where the photocatalyst is only a substance, the intensity of IEF can be measured using the model developed by Kanata that proves that IEF strength is determined by surface potential and surface charge density.\(^2\)\(^5\),\(^5\)\(^1\)-\(^5\)\(^3\),\(^5\)\(^4\)

\[
E = \left( \frac{-2V_S \rho}{\epsilon\varepsilon_0} \right)^{1/2}
\]  

(Eq. 1)

\(E\), the value of internal electric field, \(V\); \(V_s\), the surface potential, \(V\); \(\rho\), the surface charge density, \(C/m^2\); \(\epsilon\), low-frequency dielectric constant; and \(\varepsilon_0\), vacuum dielectric constant, \(8.854 \times 10^{-12} \text{ F/m}\).

When the crystals are similar, the difference in \(\epsilon\) is negligible.\(^5\)\(^4\)-\(^5\)\(^6\) otherwise it can be measured with an impedance analyzer. The Equation (1) indicates that the IEF magnitude is mainly determined by the surface voltage and the charge density.

The \(V_s\) can be detected by atomic force microscopy (AFM) with Kelvin probe force microscopy (KPFM) model or open circuit voltage.\(^2\)\(^3\),\(^5\)\(^7\)-\(^6\)\(^0\) KPFM is based on the non-contact AFM mode for detecting CPD between the work function of AFM tip and the sample, which combines the ability to simultaneously image surface morphology and surface potential with nanoscale spatial resolution and millivolt electrical resolution.\(^6\)\(^1\) As mentioned above, CPD exited due to the equilibration of the initially different Fermi levels generally leading to charging of the two materials when two different materials are brought into electrical contact. KPFM maps the CPD between a conducting AFM tip (also called the Kelvin tip) and a sample surface. The CPD between the tip and the sample are defined as:

\[
\text{CPD} = \frac{\phi_{\text{tip}} - \phi_{\text{sample}}}{e}
\]  

(Eq. 2)

where \(\phi_{\text{tip}}\) and \(\phi_{\text{sample}}\) is the work function of the tip and the sample surface.

The Fermi levels of tip and the sample are aligned by charge flow when the tip contacts the sample surface, at the same time the system reaching an equilibrium state as shown in Figure 3A. The charge flow leads to the charging of the tip and sample surfaces and an electrical force forms in the gap between the tip and sample surface (Figure 3C). Meanwhile, the vacuum levels differ and the corresponding potential difference is known as the CPD. If an applied external bias \((U_{\text{bias}})\) has the same magnitude as the CPD with opposite direction, the surface charges and the electrical force would be nullified (Figure 3B). Thus, the CPD is determined by tuning the \(U_{\text{bias}}\) to nullify the electrical force (Figure 3D). Since KPFM is a nondestructive and in situ test, it has been widely used as an effective means of characterizing the surface potential of materials.\(^2\)\(^4\),\(^5\)\(^7\),\(^5\)\(^9\),\(^6\)\(^2\)-\(^6\)\(^4\) But it should be noted that the undulation of the photocatalysts using KPFM is preferably nanoscale since governed by the probe, which increases the difficulty of testing micron-sized photocatalysts. In this situation, the open circuit voltage can be applied to test the surface potential of the photocatalyst, which is an electrochemical method thus requiring strict control of the environment for testing to make the sample comparable.

Another parameter that determines the size of the IEF is the surface charge. Here we recommend two testing methods: one method is applying simultaneous potentiometric titration and conduct metric titration to obtain the equilibrium constants K\(_1\) and K\(_2\) values of the photocatalyst. According to the equilibrium constants, the surface charge density \(\rho\) as function of pH values can be calculated by the application of Equation (3), and the change of charge density with the pH of the solution can be calculated.\(^6\)\(^5\)-\(^6\)\(^7\)

\[
\rho_0 = \left( \frac{F}{A} \right) \left[ \left( \frac{10^{-2 pH} - K_1K_2}{10^{-2 pH} + 10^{-pH}K_1 + K_1K_2} \right) N_T \right]
\]  

(Eq. 3)
F, Faraday constant; A, the total surface area; NT, the total number of moles of surface sites; K1, K2, correspond to the acid equilibria constants.

Among the Equation (3), the K1 and K2 are obtained according to Henderson-Hasselbach:

\[ pH = pK_1 + \log \frac{[MOH]}{[MOH]^+}, \quad pH = pK_2 + \log \frac{[MO^-]}{[MOH]} \quad (4) \]

The other method to obtain the surface charge density of the photocatalyst is to use the Gouy-Chapman model shown below:

\[ \sigma = \sqrt{8kT\epsilon_0n\sinh \left( \frac{Z\epsilon_0\psi_0}{2kT} \right)} \quad (5) \]

σ, surface charge density, C/m²; k, the Boltzmann constant, J · K⁻¹; T, absolute temperature, K⁻¹; ε, Relative medium constant; n, Number of electrolytes per unit volume, m⁻³; e₀, electron charge, C; z, Electrolyte valence; ψ₀, Surface potential, V.

Among the Equation (5), for the smaller Zeta potential value (ψ₀ < 50 mV), there is an approximately Equation (6):\(^{51-53,69,70}\):

\[ \psi_0 = \zeta (1 + D/a_1) \epsilon D \quad (6) \]

a₁, Particle Stokes radius, m; ζ, zeta potential; κ⁻¹, Debye length, nm; and D, Distance from Sliding Layer to Particle Surface.

The above formulas indicate that the surface charge is determined by the zeta potential because the difference of other parameters is weaker than that of zeta potential for the case of crystals with similar structures. So far, the surface potential and surface charge density have been obtained. According to Equation (1), the IEF of photocatalyst can be calculated.

We have applied KPFM and zeta potential to determine the IEF of single bismuth oxyiodide with various crystal structures (BiOI, Bi₄O₅I₂, and Bi₅O₇I) recently.\(^{47}\) Firstly, the surface potential of samples prepared was measured by KPFM (Figure 4A-C). The two-dimensional field of the surface potential distribution showed obvious difference among samples. The surface potential distributions of BiOI, Bi₄O₅I₂, and Bi₅O₇I were −200 − −290, −315 − −335 and −380 − −410 mV, respectively (Figure 4D). Secondly, Zeta potential was used to measure the potential of samples prepared in BPA and water environments, and the results were agreed with the trend of surface potential measured by AFM in air (Figure 4E). Then, the surface charge density was calculated according to the Zeta potential (Figure 4F). Finally, after calculation, it was found that the IEF of Bi₅O₇I was 1.6 times and 3.4 times stronger than that of Bi₄O₅I₂ and BiOI, respectively (Figure 4G).

4.2.2 IEF measurement of composite photocatalyst

For a composite photocatalyst in which an IEF is present at the interface formed between two substances, the surface potential of the two substances can be tested by KPFM and then the interface IEF value can be obtained by differentiated the surface potential difference. Gao et al. used KPFM to probe the interface of a model phase junction composed of rutile nanorods (NRs) and anatase nanoparticles (NPs), providing a typical method for testing the interface IEF values of composite photocatalyst structures.\(^{71}\) Figure 4H shows a well-defined interface between rutile NRs arrays and anatase NPs. The 3D surface potential at the interface of TiO₂ phase junction in

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**FIGURE 3** Energy level diagram, A, and schematic model of the AFM tip contacts the sample surface, C. Energy level diagram, B, and schematic model of the tip and the sample surface, D, for the case of applying a bias (Ubias) which has the same magnitude as the CPD with opposite direction to invalidate the surface charge. AFM, atomic force microscopy.
Figure 4I exhibits obvious difference between NRs and NPs. The Fermi level of the rutile and anatase sample was aligned at the thermal equilibrium state. The CPD represents the variation of the local vacuum energy level relative to the Fermi level across the TiO$_2$ phase junctions. The cross section of the surface potential in Figure 4J shows that the work function of rutile is 30 mV higher than that of anatase, forming an interface IEF.
from anatase to rutile across the rutile/anatase junction. The strength of the IEF was obtained by differentiating the fitted profile in Figure 4J and the maximum electric field was calculated to be \(-1 \text{ kV cm}^{-1}\) (Figure 4K). Therefore, the interface IEF of a composite photocatalyst can be visually represented by KPFM.

5 | APPLICATIONS OF IEF ENGINEERING IN PHOTOCATALYTIC ACTIVITY ENHANCEMENT

In the above, we have identified the source of IEF, given the strategies of enhancing IEF, and established the test methods to quantify IEF. Next, we will focus on the application of IEF in photocatalysis (Figure 5), and based on these examples, further reveal the mechanism of the IEF engineering effectively steering the separation of photogenerated charges, thereby significantly improving photocatalytic.

5.1 | Unit cell structure of crystal for tuning the IEF

The intensity of the local IEF of the unit cell changes when the change of the crystal structure affects the positive and negative electric centers of the unit cell, therefore IEF can be adjusted by the crystal structure to realize steering photogenerated charge. In our study of BiPO₄ photocatalysts with different crystal structures, the dipole moments of the PO₄ tetrahedron in hexagon BiPO₄ (P₃₁2₁, HBIP), monoclinic BiPO₄ (P2₁/m, mMBIP) and monoclinic BiPO₄ (P2₁/n, nMBIP) were calculated from the center of gravity of the oxygen ion in the PO₄ tetrahedron. The dipole moment and the photocatalytic reaction rate are shown in Figure 6A. The results reveal that nMBIP changes the distribution of electron clouds between P-O due to its distorted PO₄ tetrahedron, and the induced dipole moment promotes the separation of e⁻-h⁺ pairs, thus showing the highest activity mechanism. Adjusting the crystal structure by surface oxygen vacancies would make a difference on IEF. When Seo et al. used DFT to explore the possible mechanism of LaAlO (001) polar surface stabilization, they found that surface vacancies could easily compensate for the IEF, which is attributed to large structure relaxation caused by vacancies forming a gap state on the surface to accommodate electric charges and shield the electric field. This result indicates that IEF tuning is achieved by introducing crystal structure regulated via surface oxygen vacancies. DFT calculations indicate that the shortened crystal lattice parameter b in Bi₂MoO₆ samples could induce larger dipole moment (Figure 6B,C), which is verified by the modulation of the pH of the reaction solution during a solvothermal synthetic process. Accordingly, these Bi₂MoO₆ samples demonstrate a gradually enhanced photocatalytic performance with increasing IEF. As mentioned above, our group used bismuth oxyiodide as an example to design the crystal structure by changing the content of I element, and selected BiOI, Bi₄O₅I₂ and Bi₅O₇I with obvious structural features as the research object. Combining the DFT computations (Figure 2B) and testing results (Figure 4A-G) in section 4, it is confirmed that the IEF could be adjusted successfully by simply changing the crystal structure. Irradiated below 420 nm, the photodegradation of BPA of Bi₅O₇I is 4.65 times and 6.59 times greater than that of Bi₄O₅I₂ and BiOI (Figure 6D), respectively. Our results demonstrate that the reduction of I in bismuth oxyiodide increased dipole and crystal local IEF, thereby improving the photogenerated charge separation.

5.2 | Molecular dipole of organic compounds enhanced via introducing groups

Due to the rich resources, safer, and more environmentally friendly, organic photocatalysts have attracted more and more interest from researchers. In particularly, several organic dye molecules have been developed as
photocatalysts because of their large delocalization system and high spectrum efficiency. Moreover, the organic photocatalyst can change its molecular dipole and IEF by grafting suitable substituents, thereby positively affecting the separation of photogenerated charges.

As early as 2016, our group present that one-dimensional supramolecular organic nanofibers, which is a carboxy-substituent perylene diimide (PDI) molecule that is self-assembled by H-type π-π stacking and hydrogen bonding (Figure 7B). It is a robust and effective photocatalyst for both organic pollutants degradation and water oxidation under visible light without the addition of the metal cocatalysts. We have confirmed that one of the reasons for the high activity of this supramolecular photocatalyst is that the introduction of terminal carboxyl groups and the high electron affinity of perylene core constitute the intramolecular polarization from perylene core to imide substituents and the IEF of the supramolecular nanofibers (Figure 7D), which directly leads to an increase in light-induced charge carrier migration and separation efficiency (Figure 7A,C). These findings may help develop semiconductor-based organic supramolecular materials for environmental protection and water decomposition.

Recently, our group enhance the porphyrin molecular (PP) dipole by synthesizing different substituent-substituted porphyrins, thereby improving high photocatalytic reduction and oxidation activity. Several porphyrin derivatives are produced by different electronegative substituents such as pyridyl, cyanophenyl, and carboxyphenyl for the R positions of PP (Figure 8A). According to the calculated results
by DFT/b3lyp, 6-311G, substituents with a higher electronegativity lead to larger molecular dipoles. Tetra(4-carboxyphenyl) porphyrin (TCPP) presents the largest dipoles of 4.08 Debye among these derivatives, thereby creating a significant difference in potential between ring center and terminal substituents (Figure 8B). At the same time, owing to the aggregation, the molecular isolated energy level was liner combined into semiconductor energy band in self-assembled TCPP (SA-TCPP), exhibiting a single absorption edge of 700 nm and significantly improving the theoretical spectral efficiency of SA-TCPP to 44.4% (Figure 8C). Driven by the IEF, the photogenerated carriers generated inside the photocatalyst are separated and transported to the surface through the \( \pi-\pi \) channel, to react, thereby achieving the high photocatalytic reduction and oxidation activity. The photocurrent of SA-TCPP is as high as 3.52 \( \mu \)A cm\(^{-2} \) compared to the untreated TCPP powder, further indicating the directional movement of electrons and excellent separation of carriers in the material (Figure 8D). The introduction of IEF makes it possible to evolve hydrogen and oxygen by a metal-free porphyrin photocatalyst without cocatalyst.

5.3 | Doping tuning the IEF

Similar to grafting a substituent on an organic photocatalyst, doping a suitable element to an inorganic photocatalyst can enhance the local IEF of the unit cell, thus promoting the separation of photogenerated e\(^{-}\)-h\(^{+}\) pairs. Back in 2007, our team found that the doped fluorine (F) ions enhanced the WO\(_6\) octahedron deformation in the F-doped ZnWO\(_4\) system by increasing the coordination around the W atoms in the WO\(_6\) octahedron, thereby strengthening the local IEF further increasing photocatalytic activity.\(^{33,42,73}\) Additionally, F-doped BiWO\(_6\) demonstrated the same mechanism and further proposed that the F\(^{-}\)-containing function on the surface...
of catalyst could serve as an electron-trapping site to enhance interfacial electron-transfer rates by tightly holding trapped electrons.\textsuperscript{74,75} By doping ZnWO\textsubscript{4} with a Cl that the electronegativity is slightly weaker than F, it is again proven that the doping of strong electronegativity elements has a positive effect on the migration of photogenerated charges by changing the original charge distribution in the crystal.\textsuperscript{76} Based on these research work, we further elucidated the mechanism of F-doped enhanced photocatalytic activity in 2013 study of F-doped BiPO\textsubscript{4} photocatalysts. It reveals that the mechanism of using high electronegativity F element instead of lattice oxygen to increase the polarizability and the induced dipoles moment of BiPO\textsubscript{4}, thereby contributing to the separation of photogenerated electrons-hole.\textsuperscript{32} In addition to the doping of F and Cl elements, several commonly used non-metallic element doping also include P, S, N, B, Br, C. Li et al. examined the tuning effect of these elements on the IEF of Bi\textsubscript{3}O\textsubscript{4}Cl theoretically (Figure 2A) and experimentally (Figure 9A), demonstrating that IEF tuning due to carbon doping is an efficient strategy to improve bulk-charge separation. Through incorporating carbon into the Bi\textsubscript{3}O\textsubscript{4}Cl lattice to increase IEF, the PL intensities is quenched over 90\% (Figure 9B) and its bulk-charge separation efficiency up to 80\% (Figure 9C), which is the root cause of the significant increase in O\textsubscript{2} evolving activity (Figure 9D).\textsuperscript{23} Moreover, gradient P incorporation in the Fe\textsubscript{3}O\textsubscript{4} improves the performance of solar water splitting by enhancing charge separation.\textsuperscript{77} It’s also C element doping,
coplanar graphited carbon rings introduced into the conjugated network of $g\text{-C}_3\text{N}_4$ along different depths from the surface. The subsequent IEF facilitates greatly the $\text{e}^-\text{-h}^+$ pairs separation and transfer, thus exhibiting remarkably enhanced photocatalytic hydrogen evolution (PHE) efficiency. Since metal element doping easily induces structural defects, the doping of the metal element should also consider the effect of the defect on the electronic properties of the photocatalyst. The Ti doping designed by Lian et al. for Zn-MnO$_2$ and the resulting oxygen vacancies open the [MnO$_6$] octahedral walls. They conducted DFT calculations as shown in Figure 9E to investigate the charge density distribution around oxygen vacancy. The Ti substitution and its derived oxygen vacancy create a charge depletion zone and finally form IEF in the crystal structure. The unbalanced charge and spin distribution in the tunnel induce an IEF within the interfaces, while lopsided charge distribution around Ti substitution site and its derived oxygen vacancies lead to a local in-plane electric-field crystal structure, thus promoting ion diffusion/electron transport. Pan et al.
explained from a microscopic point that the oxygen vacancies introduced by Zn doping can effectively improve the charge separation efficiency. They introduced oxygen vacancies through Zn-doped BiVO₄, and found that the homojunction between the doped crystal and the original crystal formed a IEF, which effectively promotes charge separation and interface charge transfer (Figure 9F).³¹ In summary, doping changed the charge density distribution to achieve local unit cell IEF tuning thereby steering the migration of photogenerated charge and improving the photoactivity.

5.4 | Heterogeneous interface constructed IEF

In section 4.1 we have already mentioned that when two substances (A and B) are combined to form an interface, the difference in their work functions is the contact potential difference (CPD), which forms the interface IEF. The interface IEF drives photogenerated charge to transfer and overcomes the same charge repulsion between the conduction bands or valence bands of two semiconductors to realize directional migration of photogenerated carriers as a result reducing the recombination rate of photogenerated e⁻-h⁺ pairs. There are approximately three concepts describing this phenomenon depending on the application of the composite photocatalyst.

Firstly, the substance B acts as a charge modulator of A. For example, a photocatalyst A with narrow band gap and high photogenerated charge recombination rate is composited with a suitable work function metal oxide B to achieve the injection or extraction of charge carriers at the interface. Since the work functions are different, IEF is formed at the A/B interfaces. Considering that B does not necessarily have photocatalytic activity, B is called a charge modulator of A. We took semiconductor Bi₄TaO₈X (X = Cl, Br) and chemically inactive MoO₃ with a large work function, named charge modulator, as an example to explain the effect of IEF on the migration of photogenerated charge at the interface.⁴⁵ When MoO₃ is introduced on the surface of Bi₄TaO₈X, the electrons subsequently flow from Bi₄TaO₈X to the MoO₃ owing to the latter has a larger work function, leaving electron accumulation layer at the surface of MoO₃ and electron depletion layer at the surface of Bi₄TaO₈X. After reaching equilibrium, a strong upward band bending at the semiconductor surface is established which forms an IEF from Bi₄TaO₈X to MoO₃ at the interface (Figure 10A). Under irradiation, IEF drives the photogenerated holes to move toward MoO₃, while the photogenerated electrons move in the opposite direction, accordingly, achieving the separation of charge carriers and the promotion of photocatalytic activity (Figure 10B). The photocatalytic activity is evidently enhanced with the favor of MoO₃ on Bi₄TaO₈X, implying that the enhanced IEF owing to the

**Figure 10** A, Schematic energy levels of MoO₃ on semiconductor Bi₄TaO₈X (X = Cl, Br). B, Schematic diagram of photocatalytic water oxidation on Bi₄TaO₈X (X = Cl, Br) and MoO₃-Bi₄TaO₈X (X = Cl, Br) with enhanced band bending; 2017, Nature⁴⁵
decoration of MoO₃ does indeed improve the photocatalytic water oxidation efficiency.

Secondly, the substance B and A constitute a heterojunction A/B. For the case where the photocatalyst A and B both have photocatalytic activity in the test environment but the recombination rate of the photogenerated e⁻⁻h⁺ pairs is high. After A and B form an interface, IEF is constructed at the interface due to the difference in work function. The IEF can serve as a driving force for the photogenerated charge transfer when the energy band structure of the photocatalysts is matched to form type II and p-n heterojunction. Xie et al. deposited anatase TiO₂ film with a work function of 4.70 eV on an FTO electrode with a work function of 5.17 eV. The difference in work function establishes interface IEF, which enhances the migration rate of photoexcited charge of TiO₂ by drift.³⁴ In the past few years, our group has combined organic or inorganic photocatalysts with C3N4, and based on morphology control, constructed a series of heterojunctions with excellent photocatalytic activity: g-C₃N₄@Bi₂WO₆,⁸¹ g-C3N4@TiO₂,⁵⁵ g-C3N4@ BiPO₄,⁸² Poly-3-hexylthiophene-g-C₃N₄,⁴³ Polyaniline/g-C₃N₄,⁸³ and so forth. The above study takes g-C₃N₄ as an example and systematically to confirm the driving effect of heterojunction interface IEF on photogenerated charge migration, and simultaneously the photocatalytic performance of the two photocatalysts improved to achieve the high photocatalytic activity of the heterojunction.

Finally, the substance B acts as a cocatalyst of the main catalyst A. Selecting the semiconductor B with a suitable work function and combining it with the semiconductor A for hydrogen production and oxygen production, B can enrich the carriers due to the difference in the work function of A and B. In the circumstances B replaces the traditional expensive precious metal as a cocatalyst of A. In this way, Ran et al. selected Ti₃C₂⁴ and metal-free phosphorous⁸⁴ as cocatalysts for metal sulfide. Since the interface IEF generated by the difference in work function between the cocatalyst and the main catalyst promotes rapid migration of photogenerated carriers, excellent visible light photocatalytic hydrogen production is obtained. Although the above situation is different in application, the essence is that interface IEF formed by the difference in work function between A and B serves as a driving force for photogenerated carrier migration, thereby improving photocatalytic activity.

### 5.5 Phase junction constructed IEF

In addition to different crystal materials, the work functions of different crystal phases are also different, resulting in the presence of IEF between the junctions. In particular, polycrystalline semiconductors are quite common in nature compared to composite crystal materials, so a junction with interface IEF can be conveniently fabricated by fine-tuning the phase transformation conditions. The phase junction has been demonstrated to be an efficient approach to enhance photogenerated charge separation, which improves photocatalytic activity. As shown in Figure 4H-K, KPFM has defined that a built-in electric field with a maximum value of 1 kV cm⁻¹ is generated at the phase junction between rutile and anatase. In addition, spatially-resolved surface photovoltage spectroscopy has clearly demonstrated that electrons generated by ultraviolet light irradiation are transferred from the rutile to anatase phases under the driving of the IEF across the interface.⁷¹ Our group designed the phase structures of BiPO₄, which gradually transformed from hexagonal BiPO₄ to monazite monoclinic BiPO₄ and monoclinic BiPO₄ with increasing calcination temperature. The enhanced photocatalytic performance of the monazite monoclinic-monoclinic BiPO₄ surface-phase junction proved that the phase interface IEF accelerates the charge separation and transfer.¹¹ A phase junction over the orthogonal Bi₂SiO₅ and tetragonal Bi₂SiO₅ structures was successfully synthesized by ion exchange method. The significantly enhanced photocatalytic activity under ultraviolet light irradiation is attributed to the IEF at the crystal phase interface effectively improving the separation rate of photogenerated carriers.¹²

### 5.6 Crystal facet tuning IEF

Despite much effort in understanding the role of different facets in photocatalysis, the intrinsic reasons and processes are not yet well understood. One prevailing hypothesis is that the strength of built-in electric field is the determining factor.⁸⁵ Since the IEF is directional, the exposed facet of the crystal affects the size of the IEF. The photocatalyst's IEF can maximize the effect on the photogenerated charge separation when the exposed facet is in the direction of IEF. This is also directly proved by the surface potential difference of the various crystallographic faces of Cu₂O measured through KPFM (Figure 11A). A map of the KPFM potential (Figure 11B) and the KPFM potential overlaid on the height (Figure 11C) reveal that the highest potentials are observed on the {100} surfaces and intermediate potentials are observed on the {110} surfaces. Turning attention to the triangular pyramids, again the highest surface potentials are observed on the highly polar {001} surfaces and intermediate potentials on the {110} surfaces (Figure 11D-F).⁸⁶ Jin et al. reported a photoelectric...
obvious anisotropy between (111) and (100) facet devices of CH$_3$NH$_3$PbBr$_3$ (MAPbBr$_3$) single crystal. They found an open-circuit voltage on the (111) facet device and therefore required high voltage to overcome the built-in electric field to activate ions participating in conduction. This result indicated that different exposed crystal facet affects the IEF. The high exposure percentage of the {001} facet of BiOX (X = Cl, I) is beneficial to the effectively take advantage of the IEF to promote charge transfer and increase the photoactivity, which is evidenced by the enhanced photocurrent and quenched photoluminescence signal of the {001} facet-dominant nanosheets compared with that of the {010} facet-dominant counterparts. The spatially resolved surface photovoltage spectroscopy (SRSPS) can be used as a powerful tool for detecting the accumulation of photogenerated charges on different surfaces of the photocatalyst. Zhu et al. reveal the anisotropic photoinduced charge distributions on different facets of BiVO$_4$ single particles by SRSPS. The dark-state surface potential images of a single BiVO$_4$ crystal with exposed {010} and {011} facets clearly show the diversity of the potential within a single crystal further indicate that the two kinds of facets have different surface potential (Figure 11G,H). The surface potential is increased under irradiation (Figure 11I) and are mainly distributed on the {011} facets (Figure 11J), which undoubtedly confirms the existence of IEF and the separation of photogenerated charges on the surface of the crystal. These results directly indicate that the driving force of the photogenerated charge to the respective crystal faces varies greatly due to the difference in the relative positions of the various exposed crystal facets and the IEF direction, thus causing the accumulation of photogenerated charges on various kinds of crystal faces to be different.

5.7 | Induced polarization semiconductor materials enhanced the IEF

A non-centrosymmetric (NCS) materials refers to a type of functional material without inversion center of symmetry, which exhibit a range of important physical properties including piezoelectric, ferroelectric, thermoelectric, and nonlinear optical properties due to special structural symmetry. These materials could produce polarization electric field under suitable external electric field, pressure, temperature, and other additional conditions. Recently, a polarization electric field with the ability to promote separation of photoexcited charges was recognized by photocatalysis. BiOIO$_3$ is a nonlinear optical crystal with a strong second-harmonic generation effect ($\approx 12.5$ KDP) and a high piezoelectric coefficient of about 26 pmV$^{-1}$. It has been demonstrated that BiOIO$_3$ can be used as an efficient photocatalyst to degrade methyl orange by Wang et al. The high photodegradation activity is attributed to the local dipole moments of the IO$_3^{-}$, leading to strong macroscopic polarization along the c axis direction and driving the...
photogenerated electrons and holes in opposite directions. To further enhance the macroscopic polarization, an ionic substitution strategy by replacing I$^{5+}$ with V$^{5+}$ (Figure 12A), the strengthened SHG signals and theoretical calculations confirmed the increased of dipole moment of the IO$_3$ polyhedron (Figure 12B,C). The enhancement of macroscopic polarization largely promotes the bulk charge separation of BiOIO$_3$ both in the photocatalytic and piezoelectric catalytic processes (Figure 12D). Taking BaTiO$_3$ as a target catalyst to probe the influence of ferroelectricity on the photodegradation of Rhodamine B. BaTiO$_3$ possesses a spontaneous polarization due to the displacement of the positive and negative charge centers in the unit cell, producing a positive charge region (C$^+$) and a negative charge region (C$^-$), thereby forming a IEF from C$^+$ to C$^-$ (Figure 12E). Under the action of the IEF, the photogenerated electrons move to the C$^+$ domain and then carry out the reduction reaction, while the photogenerated holes move to C$^-$ domain and then participate in the oxidation reaction (Figure 12F). The tetragonal BaTiO$_3$ with ferroelectricity ensures efficient separation of the photoexcited carriers due to the internal space charge layer, resulting in a 3-fold increase in photodegradation of the Rhodamine B under simulated light compared to paraelectric BaTiO$_3$. It is emphasized that a polarized material having a noncentral symmetry is different from the above mentioned centrally symmetric structure for enhancing the IEF. The former’s macroscopic polarization can be directly measured by SHG, and the driving effect on photogenerated carriers is easily understood. Since the latter has central symmetry, it does not exhibit macroscopic polarization characteristics, but the IEF locally generated by the uneven distribution of positive and negative charges in the unit cell plays a decisive role in the separation of photogenerated charges.

FIGURE 12  Crystal structure of V-BiOIO$_3$ (BiOIO$_{0.926}$V$_{0.074}$O$_3$), A, along A-B and, B, along B-C planes (Black arrows indicate polarization direction of I$_{1-x}$V$_x$O$_3$). C, SHG generation for BiOIO$_3$ and BiOIO$_{0.926}$V$_{0.074}$O$_3$. D, piezoelectric catalytic processes; 2017, Wiley. Schematic of a ferroelectric material showing, E, internal polarization and screening mechanisms and, F, the effect of free carrier reorganization on band structure and photoexcited carriers. In, E, the spontaneous polarization with polarization vector P can be screened by free electrons and holes in the conduction and valence bands, respectively, and/or by ions or molecules adsorbed on the surface from the solution forming a Stern layer. In, F, the accumulation of free electrons on the C$^+$ surface and holes on the C$^-$ surface leads to downward and upward band bending, respectively. The generation of a photoexcited electron-hole pair is shown, which are separated toward opposite surfaces of the material by the internal electric field arising from the polarization. This then leads to the spatial separation of oxidation and reduction on opposite surfaces as shown; 2013, American Chemical Society.

6 | CONCLUSION

The efficient migration of photoinduced charges constitutes a key factor in photocatalytic solar energy to chemical energy conversion. Advancing photocatalysts toward high photo to chemical conversion efficiency requires efficient strategies benefited charge separation. Tracing back to the physics of the charge separation, it is the internal or surface IEF of the photocatalyst that provides the driving force. The IEF engineering has been demonstrated to be a promising strategy for steering photogenerated charge separation in photocatalytic systems recently. In this review, we traced
the source of IEF, gave the measurement of IEF and summarized the enhancement methods of IEF. As examples of IEF accelerating the separation of photogenerated charge, the application advances in IEF for photocatalysis are presented, demonstrating that IEF engineering, an important, exciting, and highly potential emerging research area, is a whole new angle of view for steering the photogenerated charge. However, due to the rising of the IEF project in the field of photocatalysis, many respects of research have yet to be improved, and future research directions should focus on the following aspects.

Firstly, significant challenges retain in the developing characterization tools for testing and quantifying IEF. In particular, in the measurement of the surface charge of photocatalyst, it is urgent to explore a universal method able to eliminate environmental interference factors and express its true surface charge.

Secondly, studies regarding theoretical calculations and modeling methods for IEF should attract much more attention. To achieve a deeper understanding of the mechanism of IEF production, the organic photocatalyst system has employed the dipole moment as an evaluation standard, but for the inorganic photocatalytic system, an evaluation standard of the local IEF in the unit cell needs to be further established.

Thirdly, the relationship between IEF and band alignment in the interface system for photogenerated charge migration needs to be clarified. For the photocatalysts forming the interface, IEF, and band alignment are the key factors driving the photogenerated charge migration. So far, few studies have considered the influence of both, especially the design and synthesis of interface to make both play a synergistic role in promoting the separation of photogenerated charge.

Finally, further development of methods for designing IEF projects used in photocatalysis is one of the critical research objectives. Considering that the existing design methods are limited, it is highly desirable to deepen the understanding of the IEF and study the enhancement methods. At the same time, consideration should be given to the photocatalytic activity of visible light driving, high solar energy conversion efficiency, proper band structure, and stability requirements.

In conclusion, we focused on the utilization of IEF engineering that is an emerging and clearly viable route to increasing photocatalytic efficiency by facilitating charge separation and transfer, thus allowing the e⁻ and h⁺ to rapidly participate in reductive and oxidative reactions, respectively. We hope this review proves a useful reference for developing high performance photocatalytic materials in the future, as well as provides a better understanding of the mechanisms for the movement of charges. This review may also stimulate further exploration involving charge regulation in solar cells, batteries, and other important research areas.

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