

# Perspective on Defective Semiconductor Heterojunctions for CO<sub>2</sub> Photoreduction

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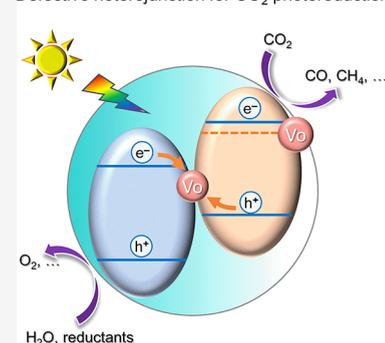
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**ABSTRACT:** Photocatalytic CO<sub>2</sub> reduction to value-added chemicals is a green solution to concurrently address CO<sub>2</sub> emission and energy issues, and semiconductor heterojunctions hold great potential to achieve such conversion. However, the photocatalytic performance of the existing heterojunctions is limited by the low interfacial charge transfer efficiency and sluggish surface reaction kinetics. To overcome these obstacles, defect engineering has been applied to heterojunctions to boost CO<sub>2</sub> photoreduction in the past 5 years. This perspective summarizes the key roles and the related mechanism of various anion vacancies located at the surface, interface, and both surface and interface of heterojunctions in photocatalytic CO<sub>2</sub> reduction. Challenges in constructing and characterizing defective heterojunctions as well as in promoting their CO<sub>2</sub> photoreduction activity and hydrocarbon selectivity are then outlined. Finally, some solutions to the rational design of defective heterojunctions for efficient and stable CO<sub>2</sub> photoreduction are also proposed.

Defective heterojunction for CO<sub>2</sub> photoreduction



## INTRODUCTION

The conversion of CO<sub>2</sub> to high value-added chemicals, such as alkanes and carbohydrates, on semiconductors by solar energy is receiving more attention because of the high demand on both suppressing greenhouse effects and developing sustainable energy sources. CO<sub>2</sub> is a linear nonpolar molecule with a C=O dissociation energy of  $\sim 751 \text{ kJ mol}^{-1}$ , making it difficult to be chemisorbed and activated on most semiconductors.<sup>1</sup> Additionally, the conversion of CO<sub>2</sub> involves complex reaction kinetics accompanied by multielectron and multiproton transfer.<sup>2</sup> Therefore, it remains a challenge to design semiconductors to achieve efficient photocatalysis toward CO<sub>2</sub> reduction.

Various metal compounds, such as metal oxides and sulfides (TiO<sub>2</sub>, CdS, and so on), are the most widely used semiconductors for CO<sub>2</sub> photoreduction, and their shortcomings limit their applications.<sup>2</sup> A single-component compound has a fixed band gap ( $E_g$ ), showing a limited response to the solar spectrum, in particular, the visible light. Also, the photogenerated electrons and holes recombine rapidly before they reach the surface of the semiconductor and participate in surface reactions. In addition, inorganic semiconductors generally have a small proportion of the exposed surface and thus poor adsorption and catalytic sites for CO<sub>2</sub> molecules. These drawbacks together result in relatively low photocatalytic CO<sub>2</sub> reduction activity. Alternatively, heterojunctions composed of two or more semiconductors with an atomic-level interface become more promising candidates for performing efficient photocatalysis due to the following merits.<sup>3</sup> (i) An alterable constitution enables a wide

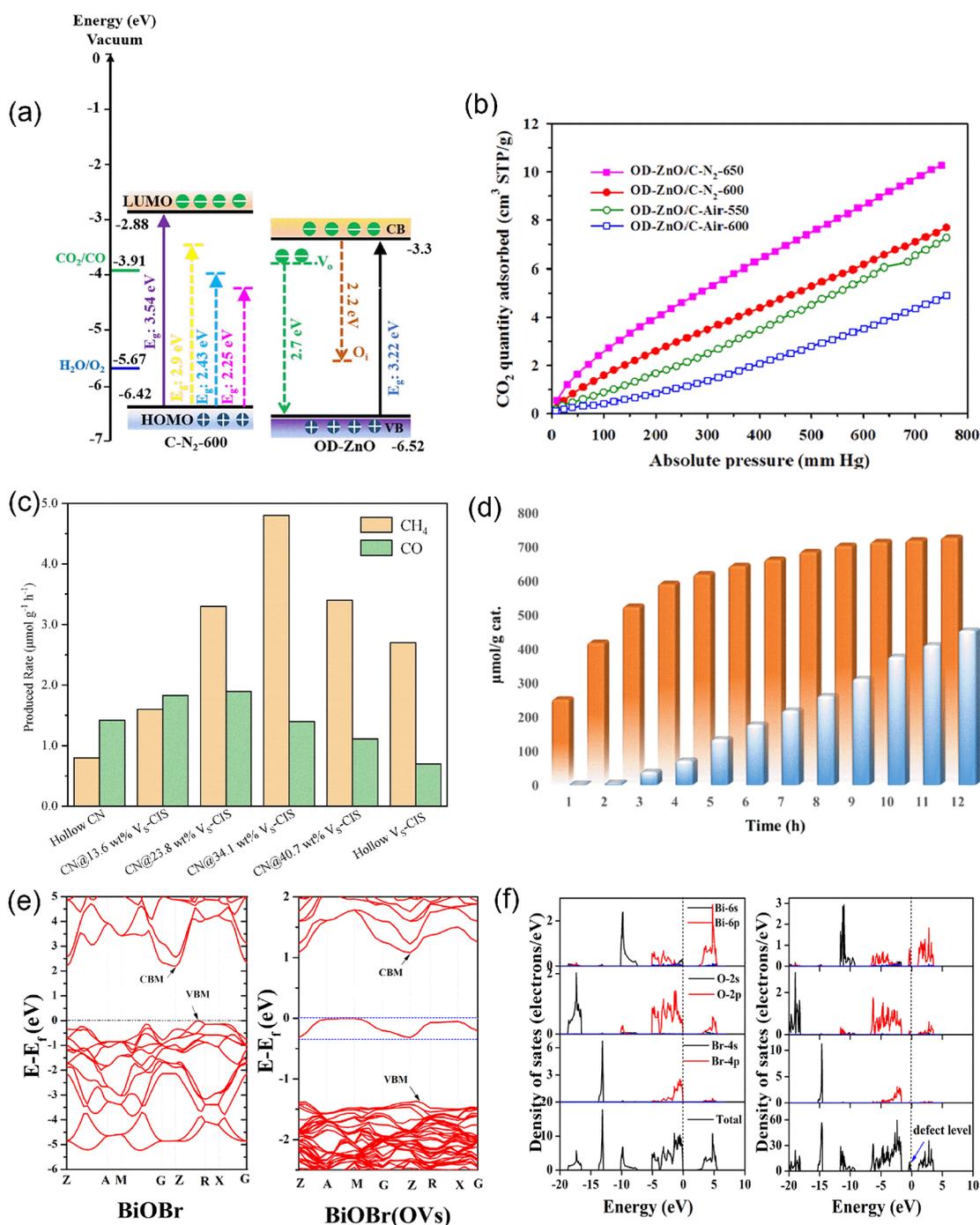
visible-light response. (ii) The difference in band edges or the Fermi level ( $E_f$ ) between the components causes band bending at the atomic-level interface, which drives the migration of electrons and holes between components in opposite directions. The cross-interface separation of charge carriers remarkably reduces their combination rate. (iii) The spatial separation of redox sites promotes forward reactions and suppresses backward ones. Numerous efforts have been made to construct heterojunctions to boost CO<sub>2</sub> photoreduction (see the related review<sup>4</sup>); however, the photocatalytic activity of existing heterojunctions is unsatisfactory, mainly due to their low interfacial charge transfer efficiency as well as sluggish surface reaction kinetics.<sup>2,5,6</sup>

Structure defects, such as point defects (cation or anion vacancies), line defects (dislocations), facet defects (grain boundaries), and volume defects (holes), are common in prepared materials, while their contents are too low to have an effect on photocatalysis. When abundant defects, such as the most common anion vacancies, are created on the surfaces of semiconductors, their great potential on boosting photocatalysis emerges. It has been found that defect engineering is a versatile means to improve the photocatalysis process from multiple aspects. There are at least three roles of defects for

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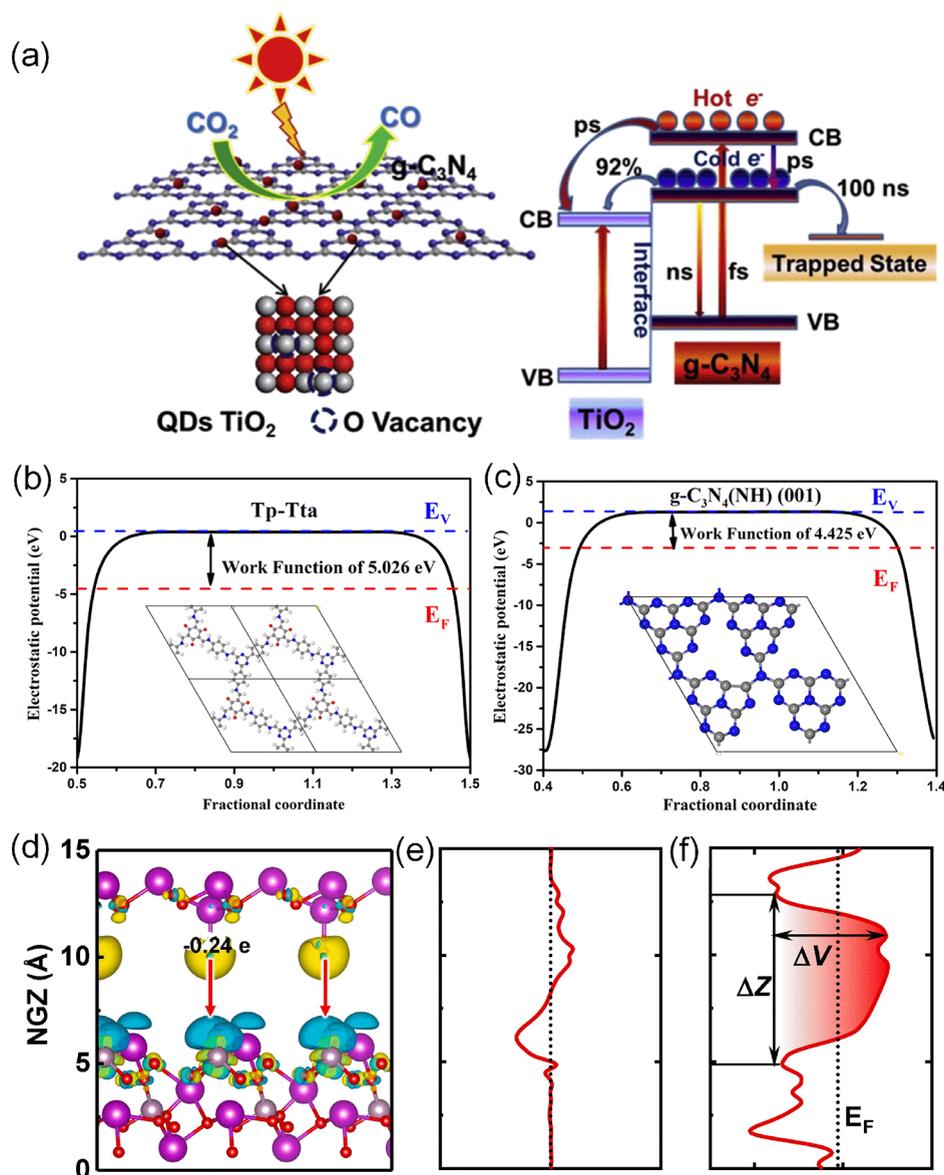




**Figure 1.** (a) Band structures and (b) CO<sub>2</sub> physisorption isotherms of OD-ZnO/C-N<sub>2</sub>-600. Reproduced with permission from ref 9. Copyright 2020 Elsevier. (c) Photocatalytic product generation rates over hollow g-CN, the CN@V<sub>5</sub>-CIS heterojunction with different contents of V<sub>5</sub>-CIS nanosheets, and hollow V<sub>5</sub>-CIS nanosheets for 6 h of illumination. Reproduced with permission from ref 11. Copyright 2021 Elsevier. (d) Time-dependent photocatalytic experiment of CO<sub>2</sub> using the 3D Y@S TiO<sub>2-x</sub>/LDH architecture. Reproduced with permission from ref 12. Copyright 2019 American Chemical Society. (e) Calculated band structure of pure BiOBr (left) and BiOBr with V<sub>O</sub> (right) and (f) calculated DOS of pure BiOBr (left) and BiOBr with V<sub>O</sub> (right). Reproduced with permission from ref 14. Copyright 2020 Elsevier.

photocatalysis:<sup>7</sup> (i) introducing defect states between conduction and valence bands of semiconductors, which reduces the  $E_g$  and thus extends the visible-light response; (ii) acting as trap centers for photogenerated carriers to delay their combination; and (iii) engineering adsorption and catalytic sites for inert molecule conversion. The detailed preparation and characterizations of defects were discussed in the related reviews.<sup>7,8</sup>

In the past 5 years, defect engineering has been successfully applied to heterojunctions to boost the CO<sub>2</sub> photoreduction, and measurable progress was made. In this Perspective, we focus on the representative studies on defective heterojunctions for CO<sub>2</sub> photoreduction in terms of defect locations (at the surface, interface, and both the surface and interface of heterojunctions). The main challenges in the design and construction of defective heterojunctions are discussed, and



**Figure 2.** (a) Proposed schematic of the band alignment of  $\text{TiO}_{2-x}/\text{g-C}_3\text{N}_4$ . Reproduced with permission from ref 16. Copyright 2021 Elsevier. Electrostatic potentials of (b) Tp-Tta COF (001) and (c) the defective  $\text{g-C}_3\text{N}_4$  (001) surface. Reproduced with permission from ref 17. Copyright 2021 Elsevier. (d) Calculated charge density difference, (e) plane-averaged charge-density difference, and (f) plane-averaged electrostatic potential along the Z direction of  $\text{Bi}_2\text{MoO}_6/\text{BiO}_{2-x}$  models with Mo–O–Bi bonds. Reproduced with permission from ref 18. Copyright 2021 Elsevier.

some opportunities for defect engineering of heterojunctions are proposed as well.

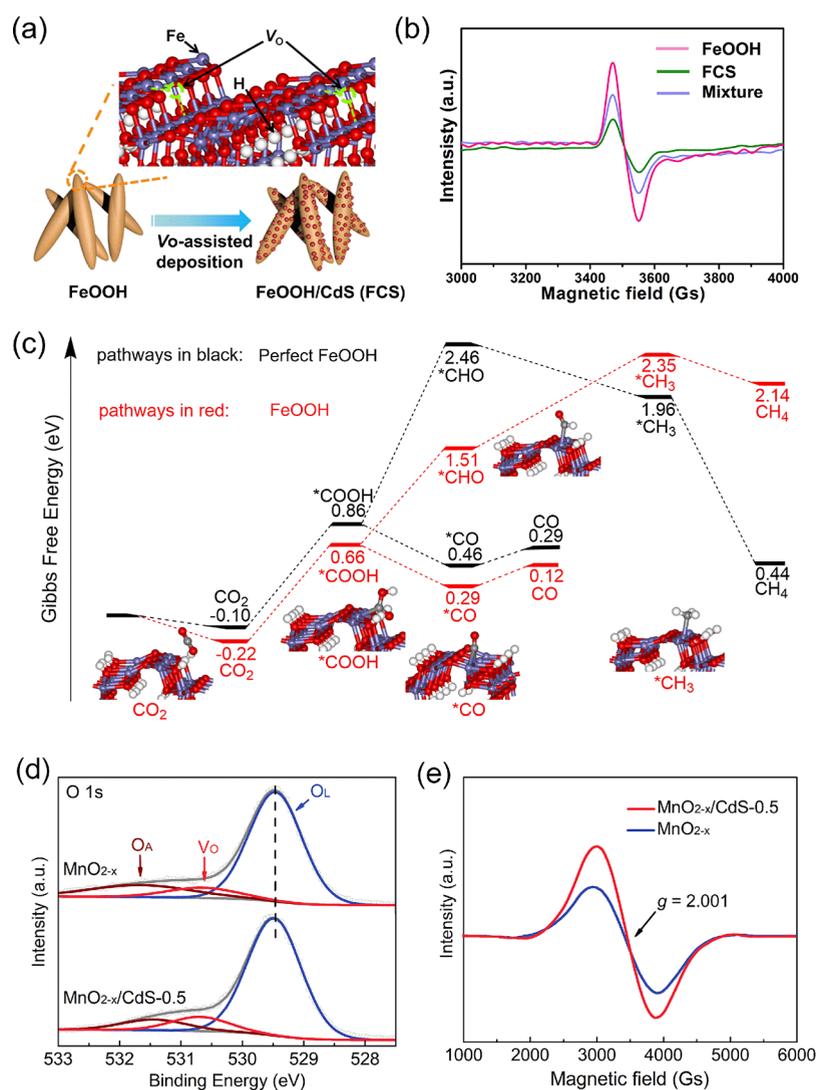
## ■ HOW THE DEFECTS MATTER FOR $\text{CO}_2$ PHOTOREDUCTION

**Surface Defects.** As mentioned above, the lack of adsorption and catalytic sites on semiconductor surface is a key factor hampering the  $\text{CO}_2$  conversion efficiency. In this regard, methods of downsizing and constructing hollow/porous structures are often taken to monotonously increase the number of active sites, while defect engineering increases the density of active sites by creating cation/anion vacancies on the surface of semiconductors. The vacancies not only offer abundant active sites for the adsorption and activation of  $\text{CO}_2$  molecules but also effectively modulate the electronic band structure of the whole heterojunction, including  $E_g$ , the conduction band minimum (CBM), and the valence band

maximum (VBM) potential. As a result, a synergistic effect of surface vacancies and heterojunctions on  $\text{CO}_2$  photoreduction is attained.<sup>9–14</sup>

It was reported that oxygen vacancies ( $V_{\text{O}}$ s) in the ZnO/carbon dot (OD-ZnO/ $\text{C-N}_2$ -600) hybrid not only extend the adsorption spectrum to the near-infrared region but also facilitate  $\text{CO}_2$  enrichment (Figure 1a,b).<sup>9</sup> More importantly, the  $V_{\text{O}}$ s with abundant trapped electrons inject free electrons into the adsorbed  $\text{CO}_2$  molecule, resulting in the bending of the O–C–O angle and the formation of the  $\text{CO}_2^-$  anion, where its degree of bending further affects the electron transfer between the semiconductor and the adsorbed  $\text{CO}_2$ .

Surface  $V_{\text{O}}$  also improves the photocatalytic activity and affects the selectivity of products in  $\text{CO}_2$  photoreduction. For instance, the  $\text{C}_1$  compound (that is, CO and  $\text{CH}_4$ ) evolution rate of the BiOBr- $\text{g-C}_3\text{N}_4$  heterojunction is promoted by the one-time creation of  $V_{\text{O}}$  on the catalyst surface.<sup>10</sup> Liu et al.



**Figure 3.** (a)  $V_O$ -assisted construction of the FCS heterostructure. (b) EPR spectra of the FeOOH nanoshuttles, FCS heterojunctions, and the mixture of FeOOH nanoshuttles and CdS nanocrystals. (c) Gibbs free energy for the  $CO_2$  reaction pathways on the pristine- and  $V_O$ -FeOOH(100) facets. The red, lavender, white, and gray colors represent O, Fe, H, and C atoms, respectively. Reproduced with permission from ref 23. Copyright 2021 Elsevier. (d) O 1s high-resolution spectrum and (e) EPR spectra of the bare  $MnO_{2-x}$  and  $MnO_{2-x}/CdS-0.5$  prepared by the photodeposition method. Reproduced with permission from ref 24. Copyright 2021 Elsevier.

found that the  $CO$  selectivity over  $CH_4$  remarkably varies with the amount of sulfur vacancy ( $V_S$ )-rich  $CuIn_2S_8$  loaded on  $g-C_3N_4$  (denoted as  $CN@V_S-CIS$  in Figure 1c).<sup>11</sup> A similar phenomenon was also observed on the three-dimensional yolk@shell hydrogenated  $TiO_2/Co-Al$ -layered double hydroxide (3D  $Y@S TiO_{2-x}/LDH$ ) architecture by Ziarat et al., who argued that the main product of photocatalytic  $CO_2$  reduction was changed from  $CH_3OH$  to  $CH_4$  after 2 h (Figure 1d).<sup>12</sup> Although the related mechanism was not addressed, one can infer that the selectivity evolution is the result of electronic structure modulation caused by an overall variation of component constitution and  $V_S$  concentration in the heterojunction. This work hints that the product selectivity of  $CO_2$  photoreduction over heterojunctions can be effectively regulated through electronic structure refinement by surface vacancies.

In addition, the effects of surface defects on the enhanced separation of photogenerated electron–hole pairs need to be identified. Recently, our group demonstrated that the presence of  $V_O$  in protonated  $g-C_3N_4/InVO_4$  ( $p-C_3N_4/InVO_4$ ) hetero-

nanobelts not only promotes the adsorption and activation of  $CO_2$  molecules on the hybrid by employing in situ Fourier transform infrared spectroscopy (in situ FTIR) but also enhances the electronic conductivity of the  $InVO_4$  component by increasing the density of the minority carrier.<sup>13</sup> Miao et al. investigated the effects of  $V_O$  on the electronic band structure of the  $AgBr/BiOBr$  heterojunction and found that surface  $V_O$  tunes the electronic band structure of  $BiOBr$  from multiple aspects. Specifically,  $V_O$  increases the hybridization of atomic orbitals, in addition to the introduction of a defect state between the CBM and VBM (Figure 1e,f).<sup>14</sup> These changes cause the electronic band structure in  $BiOBr$  to become denser, favoring the transfer of photogenerated carriers in the semiconductor. Moreover,  $V_O$  also smoothens the VBM of  $AgBr/BiOBr$ , which reduces the recombination rate of photogenerated electron–hole pairs in the heterojunction.

**Interface Defects.** Efficient interfacial charge transfer between components is essential to sufficiently enhance the photocatalytic activity of heterojunctions. For this purpose, the Z-scheme heterojunction with great potential has been

ungraded and regenerated from traditional modes with the redox shuttle to all-solid-state modes with a solid electron conductor and to a direct Z-scheme system (also called an S-scheme system). (See the related review.<sup>3</sup>) An S-scheme heterojunction is composed of reduction photocatalysts (RP) and oxidation photocatalysts (OP) with direct and intimate contact, staggered band structure, and a distinct charge-transfer route, maintaining a strong redox potential for photocatalysis. In the past few years, numerous efforts have been devoted to constructing S-scheme heterojunctions for CO<sub>2</sub> photoreduction, and it was found that high interface transfer resistance is a bottleneck for their applications in photocatalysis.<sup>2,5,6</sup>

Recently, Chen et al. pointed out that interface V<sub>O</sub> enhances the electronic interactions between g-C<sub>3</sub>N<sub>4</sub> and BiOCl in their hybrids and thus provides a fast channel for interface charge transfer, leading to a significant enhancement for photocatalytic CO<sub>2</sub> reduction activity relative to that without V<sub>O</sub>.<sup>15</sup> The related mechanism was further investigated by other groups, and three kinds of effects associated with interface V<sub>O</sub> in photocatalysis were revealed successively: (i) The introduction of the defect state as electron-trap sites to boost interface charge transfer and to promote CO<sub>2</sub> activation. Shi et al. demonstrated that charge transfer occurs from 2D-g-C<sub>3</sub>N<sub>4</sub> to 0D-TiO<sub>2</sub> on an ultrafast subpicosecond time scale (<1 ps) through an intimate interface (Figure 2a,b).<sup>16</sup> The ultrafast interface charge transfer in the TiO<sub>2-x</sub>/g-C<sub>3</sub>N<sub>4</sub> hybrid is related to the recombination relaxation mediated by shallow trapped sites created by V<sub>O</sub> in the TiO<sub>2</sub> component, which greatly facilitates charge separation, while the electrons in shallow trapped sites are easily trapped by CO<sub>2</sub> absorbed at the defect sites. (ii) Modulating E<sub>f</sub> to enhance the interfacial built-in electric field.<sup>17</sup> Ye et al. pointed out that nitrogen vacancies (V<sub>N</sub>) lift the E<sub>f</sub> of g-C<sub>3</sub>N<sub>4</sub> and thus widen the E<sub>f</sub> gap between g-C<sub>3</sub>N<sub>4</sub> and Tp-Tta COF (Figure 2b,c). As a result, a stronger built-in electric field was formed at the interface, promoting the recombination of invalid photogenerated carriers through the S-scheme pathway. Besides, both the stability and deactivation of interface V<sub>N</sub> are also improved. (iii) Bridging components via chemical bonding. Zhu et al. suggested that the presence of V<sub>O</sub> in BiO<sub>2-x</sub> favors the insertion of O atoms from Bi<sub>2</sub>MoO<sub>6</sub> component into the vacancy sites, and thus the construction of interfacial electron-transport bridge between the two components (Figure 2d-f).<sup>18</sup> The bond bridge significantly enhances interfacial electronic interaction and effectively inhibits the charge recombination and deactivation of pristine Bi<sub>2</sub>MoO<sub>6</sub>.

Notably, interface vacancy is likely to associate with the transformation of electron transfer routes, from type-II to S-scheme in general, since several reports have demonstrated that many thermodynamically favorable type-II systems operate in terms of S-scheme transfer mechanism because of the presence of anion vacancies, such as g-C<sub>3</sub>N<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub> hybrid with interface V<sub>O</sub>,<sup>19</sup> g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> with interfacial V<sub>N</sub> and V<sub>O</sub> dual vacancies,<sup>20</sup> and BiO<sub>1-x</sub>Br/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>.<sup>21</sup> Although the S-scheme charge-transfer pathways of these defective heterojunctions were experimentally verified, the correlations of the charge transfer pathway with the interface vacancy were not well addressed yet, for which the mechanism is the key to rationally constructing S-scheme systems. There remain great opportunities to explore the roles of vacancies in the formation of S-scheme heterojunctions, and more studies need to be carried out.

**Both Surface and Interface Defects.** The above analyses hint that the combination of surface and interface defects may

be an alternative way to further release the potential of heterojunctions for CO<sub>2</sub> photoreduction. It has been found that the defect-induced selective deposition strategy offers the possibility of constructing such heterojunctions with both surface and interface defects.<sup>22,23</sup> However, little attention was paid to the coexistence effect, possibly because of the difficulty in distinguishing defects at different sites.

Our group recently reported a V<sub>O</sub>-assisted construction strategy by which CdS nanocrystals were selectively deposited at parts of the surface V<sub>O</sub> of FeOOH nanoshuttles.<sup>23</sup> The electron paramagnetic resonance (EPR) spectrum shows that the covered V<sub>O</sub> was introduced into the interfaces of the FeOOH/CdS (FCS) hybrid to enhance interfacial charge transfer while the uncovered surface V<sub>O</sub> was still exposed to act as adsorption and activation sites for CO<sub>2</sub> molecules (Figure 3a,b). Density functional theory (DFT) calculations and X-ray photoelectron spectrum (XPS) analysis confirmed that the presence of V<sub>O</sub> favors the deposition of CdS nanocrystals at the V<sub>O</sub> sites of FeOOH and endows the formed FCS heterojunction with a strong interfacial charge difference. Moreover, the surface V<sub>O</sub> thermodynamically favors the conversion of CO<sub>2</sub> to CO by reducing the formation energy of key intermediate products, i.e., COOH\* (Figure 3c). Benefiting from the synergistic effects of both surface and interface V<sub>O</sub> and a type-II system, the optimized FCS heterojunction displays a C<sub>1</sub>-compound production rate of 18.43 μmol g<sup>-1</sup> h<sup>-1</sup> (5.88 μmol g<sup>-1</sup> h<sup>-1</sup> for CH<sub>4</sub>, 12.55 μmol g<sup>-1</sup> h<sup>-1</sup> for CO), about 6.2 and 8.5 times higher than for the separated counterparts under visible-light irradiation.

## ■ CHALLENGES AND OPPORTUNITIES FOR DEFECTIVE HETEROJUNCTIONS FOR CO<sub>2</sub> PHOTOREDUCTION

Although numerous defective heterojunctions have been constructed to boost the photocatalysis efficiency toward CO<sub>2</sub> reduction, their potential has not been sufficiently released yet because of the following issues:

**Precise Fabrication of Defective Heterojunctions.** The type, concentration, and distribution of defects in each component are key factors governing the photocatalytic performance and should be accurately adjusted, which highly depends on the specific methods of creating the defect. Some chemical reduction processes at high temperature or under mild conditions have been successfully applied to create surface vacancies. However, a detailed investigation and specific guideline are still lacking in precise vacancy control. Meanwhile, more cost-effective green methods should be developed. For example, the photodeposition method was recently employed by our group to increase the V<sub>O</sub> content in MnO<sub>2-x</sub> nanowires by depositing CdS NCs on its surface (Figure 3d,e).<sup>24</sup> Zeta potential and cyclic voltammetry measurements confirmed that the V<sub>O</sub> increment stems from the tripartite reaction of photogenerated holes, methanol, and surface lattice oxygen in the photodeposition process.

In theory, the preparation strategy of defective heterojunctions can be generally divided into three categories: the introduction of a defect into a presynthesized semiconductor component, creating a defect during the synthesis of a heterojunction, and slight reduction after the construction of a heterojunction. The first and second ones have been reviewed in a recent report by Xiong et al.<sup>7</sup> It is notable that the first strategy holds the potential to construct a heterojunction with both surface and interface defects by the

defect-induced selective deposition of a semiconductor on another one, as shown in Figure 3a, to which more attention should be paid. The second one involves the overall regulation of defect and heterogeneous components, which corresponds to a facile fabrication, but it is difficult to separately and sufficiently refine defects and components to attain the optimal configuration. The third one benefits from the concurrent creation of two different defects with various concentrations, depending on the specific reaction thermodynamics and kinetics in the reduction process. That is, dual defects may be formed to concurrently accelerate the two photoreduction and photooxidation half-reactions, synergistically boosting the whole photocatalysis efficiency.

**Targeted Design of a Defective Heterojunction for CO<sub>2</sub> Photoreduction with H<sub>2</sub>O.** Water is the most economical reductant in providing hydrogen atoms for CO<sub>2</sub> photoreduction. The splitting of H<sub>2</sub>O to H<sub>2</sub> and O<sub>2</sub> involves a four-electron transfer process, suffering from sluggish kinetics, which seriously hampers the photooxidation half-reaction. As a result, the photocatalysis efficiency of CO<sub>2</sub> and H<sub>2</sub>O is relatively low. It was found that the H<sub>2</sub>O dissociation is kinetically favored at a low-coordination V<sub>O</sub> site on the surface of metal-based photocatalysts, leading to the formation of bridging OH species.<sup>9</sup> Experimental and theoretical studies have demonstrated that V<sub>O</sub> plays an important role in promoting the dissociation of H<sub>2</sub>O molecules to produce active H atoms and in acting as an atomic hydrogen reservoir.<sup>25</sup> Note that different vacancies have different activation and dissociation capacities of H<sub>2</sub>O. Hence, it may be an important direction for boosting CO<sub>2</sub> photoreduction with H<sub>2</sub>O by implanting different surface defects in each heterojunction component to concurrently accelerate the two half-reactions: CO<sub>2</sub> reduction and H<sub>2</sub>O oxidation. That is, the targeted defective heterojunction possesses dual surface defects, where one is used to enhance CO<sub>2</sub> photoreduction and the other is used to promote H<sub>2</sub>O photooxidation. However, there are few reports on such a defective heterojunction for CO<sub>2</sub> photoreduction.

**Defect Engineering of Heterojunctions for Selective CO<sub>2</sub> Conversion to Hydrocarbons.** Xie et al. have recently found that the dual-metal sites (CuIn<sub>5</sub>S<sub>8</sub>) hold great potential in boosting the conversion of CO<sub>2</sub> to CH<sub>4</sub>, and sulfur vacancies (V<sub>S</sub>) further promote the CH<sub>4</sub> selectivity as well as activity by refining the electronic structure of dual-metal sites.<sup>1</sup> Afterward, more dual-metal compounds, including MgIn<sub>2</sub>S<sub>4</sub>, ZnIn<sub>2</sub>S<sub>4</sub>, and CuInS<sub>2</sub>, were found to be active in photocatalytic CO<sub>2</sub> to hydrocarbons, including CH<sub>4</sub>, CH<sub>3</sub>OH, and HCOOH.<sup>26–28</sup> However, the effects of defects on the electronic structure of dual-metal sites and their photocatalytic performance have not yet been sufficiently explored. Hence, engineering the defects of heterojunction-containing dual-metal sites via a combined experimental and theoretical approach may be a promising solution to promoting the hydrocarbon selectivity in the CO<sub>2</sub> photoreduction process.

**Stability of Defective Heterojunctions.** Surface anion vacancies endow the defective semiconductor with a certain reduction property, while the active properties allow them to be easily oxidized and filled during the photocatalytic process, thus resulting in the deactivation of the photocatalysts in several hours. Although some technologies have been proposed to regenerate defects, the additional procedure increases the process complexity and cost of the photocatalysis system, making defective heterojunctions impractical. Hence, it is

important to design defective heterojunctions with high stability, but this is still a challenge. Recently, it was found that the surface V<sub>O</sub> in TiO<sub>2</sub> can be stabilized by Fe doping.<sup>29</sup> The heteroatoms on the surface can serve as charge-compensating species to accept electrons and thus effectively stabilize V<sub>O</sub>. Hence, constructing defective heterojunctions via heteroatom doping is a promising strategy for developing efficient photocatalysts for stable CO<sub>2</sub> reduction.

**Accurate Characterizations of Defects in Heterojunctions.** The contribution of defects to photocatalytic performance is intimately associated with their specific locations, i.e., surfaces or interfaces. Thus, an accurate identification of the location of the defects and their chemical microenvironment is vital to revealing the relationship between the defective heterojunction and its photoactivity, which may be understood by various advanced characterization tools combined with theoretical calculations. EPR is a powerful technique for detecting unpaired single electrons produced by defects within the bulk of materials and gives rise to direct evidence of the presence of various vacancies. XPS uncovers the surface element composition and its chemical state, which can also offer powerful support for the validation of surface defects. The Raman spectrum can distinguish the surface and bulk V<sub>O</sub> for defective TiO<sub>2</sub> when the material is separately excited by visible light and UV.<sup>30</sup> However, the feasibility of this method in identifying the location of defects for other semiconductors deserves investigation.

Notably, it is still difficult to accurately quantify the defects located at interfaces. Scanning tunneling microscopy (STM) and aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) are two direct and powerful tools for characterizing various defects. The limited detection area of the two techniques makes it difficult to rationally qualify these defects. Recently, Hou et al. qualified the V<sub>O</sub> content in the 0D/2D Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>/BiOCl hybrid by combining the EPR intensity and component content analyses, which may provide new insights into the precise evaluation for interface defects.<sup>31</sup> Note that the validity of this approach should be investigated and examined for other defective heterojunctions.

**Electronic Structures of Defective Heterojunctions.** It is well known that defects can greatly tune the electronic band structures of materials, especially the electronic state of surface sites. Interfacial charge transfer occurs because of Fermi equilibrium, when two semiconductors are incorporated into a heterojunction with compact interface contact. The introduction of a defect into one component changes the electronic structure and redistributes the charge density. There are two typical issues to be addressed: (i) the influence of the defects in one component on the electronic structure of the other one through the interface interaction and (ii) how to refine the electronic structure of the whole defective heterojunction for CO<sub>2</sub> photoreduction. To the best of our knowledge, little attention has been paid to the two issues to date, although they are vital to defective heterojunctions in achieving efficient photocatalysis. Recently, Ma et al. investigated the effects of interface V<sub>O</sub> on the electronic band structures of the g-C<sub>3</sub>N<sub>4</sub>/Co<sub>3</sub>O<sub>4</sub> hybrid and its components by employing DFT calculations.<sup>19</sup> It was found that, for the perfect hybrid (PCCN) and V<sub>O</sub>-containing hybrid (V<sub>O</sub>-CCN), the VBM in the interface consists of both O 2p and N 2p. However, the CBM of V<sub>O</sub>-CCN is constituted of N 2p and C 2p states, and the CBM of PCCN is contributed by N 2p, C 2p, Co<sup>3+</sup> 3d, and

O 2p states. As a result, under visible-light irradiation, almost all photoelectrons in  $\text{Co}_3\text{O}_4$  O 2p states are prone to transfer to N 2p and C 2p states in  $\text{V}_\text{O}$ -CCN, which supports the experimentally verified Z-scheme charge transfer. Accurate evaluations of electronic structures for the defective heterostructure are vital to unraveling the photocatalysis mechanism, which should provide us with guidelines to design new materials, and thus state-of-the-art quantum chemical methods should be carried out to explore the chemical microenvironment, electronic structures, charge transfer between components, and properties of the reactive sites on defective heterojunctions.

## CONCLUSIONS AND OUTLOOK

According to the basic principles of photocatalysis as well as the reduction mechanism of  $\text{CO}_2$  on semiconductors, the separation of photogenerated carriers and the surface reaction kinetics are two main bottlenecks for photocatalytic  $\text{CO}_2$  reduction. Many reports have proven that heterojunctions facilitate the charge separation and structure defects enhance the adsorption, activation, and even selective conversion of  $\text{CO}_2$ . Hence, the combination of a heterojunction and a defect is an emerging promising approach to boosting  $\text{CO}_2$  photoreduction to a new level. The promotion of photocatalytic  $\text{CO}_2$  activity greatly relies on the efficient cooperation of defects and heterojunctions. The effects of defects on photocatalysis need to be systematically investigated to attain a more compressive understanding of the rational design of defective heterojunctions. It is highly speculated that heterojunctions with a rational integration of defects, dual-metal sites, and heteroatoms hold great potential in efficient and stable  $\text{CO}_2$  photoreduction. We hope that this Perspective can provide new insights into the development of high-performance photocatalysts based on the defect engineering of the heterojunction and stimulate more research interest in the near future.

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### Notes

The authors declare no competing financial interest.

## Biographies



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## REFERENCES

- (1) Li, X.; Sun, Y.; Xu, J.; Shao, Y.; Wu, J.; Xu, X.; Pan, Y.; Ju, H.; Zhu, J.; Xie, Y. Selective visible-light-driven photocatalytic CO<sub>2</sub> reduction to CH<sub>4</sub> mediated by atomically thin CuIn<sub>5</sub>S<sub>8</sub> layers. *Nat. Energy* **2019**, *4* (8), 690–699.
- (2) Navarro-Jaén, S.; Virginie, M.; Bonin, J.; Robert, M.; Wojcieszak, R.; Khodakov, A. Y. Highlights and challenges in the selective reduction of carbon dioxide to methanol. *Nat. Rev. Chem.* **2021**, *5*, 564–579.
- (3) Xu, Q.; Zhang, L.; Cheng, B.; Fan, J.; Yu, J. S-Scheme Heterojunction Photocatalyst. *Chem.* **2020**, *6*, 1543–1559.
- (4) Zhang, W.; Mohamed, A. R.; Ong, W. J. Z-Scheme Photocatalytic Systems for Carbon Dioxide Reduction: Where Are We Now? *Angew. Chem. Int. Ed.* **2020**, *59*, 22894–22915.
- (5) Bai, S.; Jiang, J.; Zhang, Q.; Xiong, Y. Steering charge kinetics in photocatalysis: intersection of materials syntheses, characterization techniques and theoretical simulations. *Chem. Soc. Rev.* **2015**, *44*, 2893.
- (6) Cui, E.; Hou, G.; Chen, X.; Xie, M.; Zhang, F.; Deng, Y.; Wu, Y.; Yang, X. Selective Bonding Effect of Heterologous Oxygen Vacancies in Z-Scheme Cu<sub>2</sub>O/SrFe<sub>0.5</sub>Ta<sub>0.5</sub>O<sub>3</sub> Heterojunctions for Constructing Efficient Interfacial Charge-Transfer Channels and Enhancing Photocatalytic NO Removal Performances. *Langmuir* **2021**, *37*, 894–907.
- (7) Bai, S.; Zhang, N.; Gao, C.; Xiong, J. Defect engineering in photocatalytic materials. *Nano Energy* **2018**, *53*, 296–336.
- (8) Xiong, J.; Di, J.; Xia, J.; Zhu, W.; Li, H. Surface Defect Engineering in 2D Nanomaterials for Photocatalysis. *Adv. Funct. Mater.* **2018**, *28*, 1801983.
- (9) Lin, L. Y.; Liu, C.; Hsieh, T. T. Efficient visible and NIR light-driven photocatalytic CO<sub>2</sub> reduction over defect-engineered ZnO/carbon dot hybrid and mechanistic insights. *J. Catal.* **2020**, *391*, 298–311.
- (10) Liu, D.; Chen, D.; Li, N.; Xu, Q.; Li, H.; He, J.; Lu, J. Surface Engineering of g-C<sub>3</sub>N<sub>4</sub> by Stacked BiOBr Sheets Rich in Oxygen Vacancies for Boosting Photocatalytic Performance. *Angew. Chem. Int. Ed.* **2020**, *59*, 4519–4524.
- (11) Liu, S.; Chen, L.; Liu, T.; Cai, S.; Zou, X.; Jiang, J.; Mei, Z.; Gao, Z.; Guo, H. Rich S vacant g-C<sub>3</sub>N<sub>4</sub>@CuIn<sub>5</sub>S<sub>8</sub> hollow heterojunction for highly efficient selective photocatalytic CO<sub>2</sub> reduction. *Chem. Eng. J.* **2021**, *424*, 130325.
- (12) Ziarati, A.; Badieli, A.; Grillo, R.; Burgi, T. 3D Yolk@Shell TiO<sub>2-x</sub>/LDH Architecture: Tailored Structure for Visible Light CO<sub>2</sub> Conversion. *ACS Appl. Mater. Interfaces* **2019**, *11*, 5903–5910.
- (13) Wang, L.; Chen, D.; Miao, S.; Chen, F.; Guo, C.; Ye, P.; Ning, J.; Zhong, Y.; Hu, Y. Nitric acid-assisted growth of InVO<sub>4</sub> nanobelts on protonated ultrathin C<sub>3</sub>N<sub>4</sub> nanosheets as an S-scheme photocatalyst with tunable oxygen vacancies for boosting CO<sub>2</sub> conversion. *Chem. Eng. J.* **2022**, *434*, 133867.
- (14) Miao, Z.; Wang, Q.; Zhang, Y.; Meng, Y.; Wang, X. In situ construction of S-scheme AgBr/BiOBr heterojunction with surface oxygen vacancy for boosting photocatalytic CO<sub>2</sub> reduction with H<sub>2</sub>O. *Appl. Catal. B: Environ.* **2022**, *301*, 120802.
- (15) Chen, Y.; Wang, F.; Cao, Y.; Zhang, F.; Zou, Y.; Huang, Z.; Ye, L.; Zhou, Y. Interfacial Oxygen Vacancy Engineered Two-Dimensional g-C<sub>3</sub>N<sub>4</sub>/BiOCl Heterojunctions with Boosted Photocatalytic Conversion of CO<sub>2</sub>. *ACS Appl. Energy Mater.* **2020**, *3*, 4610–4618.
- (16) Shi, H.; Saran Long, S.; Hu, S.; Hou, J.; Ni, W.; Song, C.; Li, K.; Gurzadyan, G. G.; Guo, X. Interfacial charge transfer in 0D/2D defect-rich heterojunctions for efficient solar-driven CO<sub>2</sub> reduction. *Appl. Catal. B: Environ.* **2019**, *245*, 760–769.
- (17) Wang, J.; Yu, Y.; Cui, J.; Li, X.; Zhang, Y.; Wang, C.; Yu, X.; Ye, J. Defective g-C<sub>3</sub>N<sub>4</sub>/covalent organic framework van der Waals heterojunction toward highly efficient S-scheme CO<sub>2</sub> photoreduction. *Appl. Catal. B: Environ.* **2022**, *301*, 120814.
- (18) Zhu, X.; Wang, Z.; Zhong, K.; Li, Q.; Ding, P.; Feng, Z.; Yang, J.; Du, Y.; Song, Y.; Hua, Y.; Yuan, J.; She, Y.; Li, H.; Xu, H. Mo-O-Bi Bonds as interfacial electron transport bridges to fuel CO<sub>2</sub> photoreduction via in-situ reconstruction of black Bi<sub>2</sub>MoO<sub>6</sub>/BiO<sub>2-x</sub> heterojunction. *Chem. Eng. J.* **2022**, *429*, 132204.
- (19) Ma, H.; Li, X.; Fan, S.; Yin, Z.; Gan, G.; Qin, M.; Wang, P.; Li, Y.; Wang, L. In Situ Formation of Interfacial Defects between Co-Based Spinel/Carbon Nitride Hybrids for Efficient CO<sub>2</sub> Photoreduction. *ACS Appl. Energy Mater.* **2020**, *3*, 5083–5094.
- (20) Yang, X.; Liu, T.; Zhang, M.; Song, B.; Li, Q.; Yang, J. Interfacial dual vacancies modulating electronic structure to promote the separation of photogenerated carriers for efficient CO<sub>2</sub> photoreduction. *Appl. Surf. Sci.* **2021**, *551*, 149305.
- (21) Ding, J.; Dai, Z.; Qin, F.; Zhao, H.; Zhao, S.; Chen, R. Z-scheme BiO<sub>1-x</sub>Br/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> photocatalyst with rich oxygen vacancy as electron mediator for highly efficient degradation of antibiotics. *Appl. Catal. B: Environ.* **2017**, *205*, 281–291.
- (22) Zhang, S.; Si, Y.; Li, B.; Yang, L.; Dai, W.; Luo, S. Atomic-Level and Modulated Interfaces of Photocatalyst Heterojunction Constructed by External Defect-Induced Strategy: A Critical Review. *Small* **2021**, *17*, 2004980.
- (23) Li, L.; Guo, C.; Ning, J.; Zhong, Y.; Chen, D.; Hu, Y. Oxygen-vacancy-assisted construction of FeOOH/CdS heterojunction as an efficient bifunctional photocatalyst for CO<sub>2</sub> conversion and water oxidation. *Appl. Catal. B: Environ.* **2021**, *293*, 120203.
- (24) Ni, M.; Zhang, H.; Khan, S.; Chen, X.; Chen, F.; Guo, C.; Zhong, Y.; Hu, Y. In-situ photodeposition of cadmium sulfide nanocrystals on manganese dioxide nanorods with rich oxygen vacancies for boosting water-to-oxygen photooxidation. *J. Colloid Interface Sci.* **2022**, *613*, 764–774.
- (25) Zhang, Y. C.; Li, Z.; Zhang, L.; Pan, L.; Zhang, X.; Wang, L.; Fazal-e-Aleem, J. J. Role of oxygen vacancies in photocatalytic water oxidation on ceria oxide: Experiment and DFT studies. *Appl. Catal. B: Environ.* **2018**, *224*, 101–108.
- (26) Zeng, C.; Zeng, Q.; Dai, C.; Hu, Y. An oriented built-in electric field induced by cobalt surface gradient diffused doping in MgIn<sub>2</sub>S<sub>4</sub> for enhanced photocatalytic CH<sub>4</sub> evolution. *Dalton Transactions* **2020**, *49* (27), 9213–9217.
- (27) Xu, F.; Zhang, J.; Zhu, B.; Yu, J.; Xu, J. CuInS<sub>2</sub> sensitized TiO<sub>2</sub> hybrid nanofibers for improved photocatalytic CO<sub>2</sub> reduction. *Appl. Catal. B: Environ.* **2018**, *230*, 194–202.
- (28) Yang, C.; Li, Q.; Xia, Y.; Lv, K.; Li, M. Enhanced visible-light photocatalytic CO<sub>2</sub> reduction performance of ZnIn<sub>2</sub>S<sub>4</sub> microspheres by using CeO<sub>2</sub> as cocatalyst. *Appl. Surf. Sci.* **2019**, *464*, 388–395.
- (29) Bo, Y.; Wang, H.; Lin, Y.; Yang, T.; Ye, R.; Li, Y.; Hu, C.; Du, P.; Hu, Y.; Liu, Z.; Long, R.; Gao, C.; Ye, B.; Song, L.; Wu, X.; Xiong, Y. Altering Hydrogenation Pathways in Photocatalytic Nitrogen Fixation by Tuning Local Electronic Structure of Oxygen Vacancy with Dopant. *Angew. Chem. Int. Ed.* **2021**, *60*, 16085–16092.
- (30) Zhang, H.; Cai, J.; Wang, Y.; Wu, M.; Meng, M.; Tian, Y.; Li, X.; Zhang, J.; Zheng, L.; Jiang, Z.; Gong, J. Insights into the effects of surface/bulk defects on photocatalytic hydrogen evolution over TiO<sub>2</sub> with exposed {001} facets. *Appl. Catal. B: Environ.* **2018**, *220*, 126–136.
- (31) Hou, W.; Xu, H.; Cai, Y.; Zou, Z.; Li, D.; Xia, D. Precisely control interface OVs concentration for enhance 0D/2D Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>/BiOCl photocatalytic performance. *Appl. Surf. Sci.* **2020**, *530*, 147218.