Broad-Spectral-Response Photocatalysts for CO₂ Reduction

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ABSTRACT: The poor conversion efficiency of carbon dioxide photoreduction has hindered the practical application at present, and one of the prime reasons for this obstacle is the inefficient solar energy utilization of photocatalysts. Generally speaking, it is contradictory for a photocatalyst to concurrently possess the broad-spectral response and appropriate band-edge positions for constantanous carbon dioxide reduction and water oxidation. In this Outlook, we summarize a series of strategies for realizing visible-light and IR-light-driven carbon dioxide photoreduction under the guarantee of suitable band-edge positions. In detail, we overview the absorbance of visible light enabled by narrow band gaps in photocatalysts, the extended photoabsorption from UV into the visible light range induced by defect levels and dopant energy levels in photocatalysts, and a more negative conduction band and positive valence band acquired by Z-scheme heterojunctions in photocatalysts. Then, we highlight the expansive photoresponse of IR light caused by intermediate bands in semiconductor photocatalysts and partially occupied bands in conductor photocatalysts. Finally, we end this Outlook concerning more design strategies and application fields of broad-spectral-response photocatalysts.

1. INTRODUCTION

Anthropogenic emission of excessive carbon dioxide (CO₂) by the combustion of fossil fuels has threatened the global climate and human activity, while the continuous decrease of fossil fuels has also resulted in the energy shortage.¹⁻⁴ In this respect, it is highly desired to convert CO₂ into high-value-added chemicals for the purpose of simultaneous environmental protection and energy regeneration. Compared with the thermocatalytic⁵ and electrocatalytic⁶ CO₂ reduction, CO₂ reduction driven by solar energy is considered as the most competitive approach thanks to its outstanding merits of nonpollution, inexhaustibility, and nonenergy inputs.⁷,⁸ However, owing to the insufficient utilization of sunlight energy, the previously reported photocatalysts usually suffer from very low conversion efficiency, which restricts their widespread applications in CO₂ photoreduction.

It is well-known that CO₂ can be reduced into carbonaceous fuels by the photoexcited electrons in the conduction band (CB), while water (H₂O) would be oxidized into oxygen (O₂) by the photogenerated holes in the valence band (VB) of a photocatalyst in the photocatalytic system of an aqueous solution or H₂O vapor (Figure 1).⁹,¹⁰ That is to say, to successfully realize the CO₂ photoreduction, the CB position of the photocatalyst should be negative as compared to the standard potentials of CO₂ reduction (Table 1); meanwhile, its VB position should be positive as compared to the standard potential of H₂O oxidation. However, there is commonly a tremendous conflict between the sufficient sunlight energy utilization and the appropriate band edge positions of a photocatalyst. In detail, as for the most conventional wide-band-gap photocatalysts, their large band gaps enable the CB and VB positions to simultaneously meet the redox potentials of CO₂ reduction and H₂O oxidation, whereas they can only absorb the UV light that accounts for ca. 5% of the whole sunlight for CO₂ photoreduction.¹¹ With regard to the narrow-
band-gap photocatalysts, they can utilize the visible light occupying ca. 43% of solar spectrum for CO2 photoreduction; however, only few of the narrow-band-gap photocatalysts possess the suitable band edge positions for coinstantaneous CO2 reduction and H2O oxidation. More importantly, although some photocatalysts with extremely narrow band gaps can absorb the IR light that occupies ca. 52% of full sunlight, they have to photocatalyze CO2 into fuels with the aid of sacrificial agents because their band edge positions are unable to simultaneously match the standard potentials of CO2 reduction and H2O oxidation. That is to say, the use of sacrificial agents can enable the occurrence of CO2 photoreduction when the VB position of photocatalysts is negative as compared to the standard potential of H2O oxidation, while it can also accelerate the separation rates of electron–hole pairs in the valence band and thus enhance the CO2 photoreduction property. However, the sacrificial agents are usually costly and pollution-carrying; in addition, the presence of sacrificial agents also leads to the complex photocatalytic system, which is detrimental to exploring the internal mechanism of CO2 reduction. Therefore, many strategies should be developed to obtain the broad-spectral-response photocatalysts with benefitting band edge positions, with efforts to achieving efficient CO2 photoreduction in aqueous solutions or H2O vapors without the usage of any sacrificial agent.

CO2 can be reduced into carbonaceous fuels by the photoexcited electrons in the conduction band, while H2O would be oxidized to O2 by the photogenerated holes in the valence band of a photocatalyst in the photocatalytic system of aqueous solution or H2O vapor.

Up to now, there have been many reviews focusing on the selection of suitable photocatalysts and the possible catalytic mechanisms for CO2 photoreduction. However, there has never been a systematic overview on how to promote the CO2 photoreduction property through the effective utilization of solar energy. For that reason, herein, we first summarize a timely survey on how to efficaciously utilize visible light and IR light for triggering CO2 photoreduction. In other words, we overview the visible-light-driven CO2 photoreduction realized by narrow-band-gap photocatalysts with appropriate CB and VB positions. In addition, we outline that the photoresponses for the photocatalysts with satisfied band edge positions could be extended from UV into visible light regions by introducing defect levels and dopant energy levels within the forbidden band. Then, we review that more negative CB and more negative positive VB positions for simultaneous CO2 reduction and H2O oxidation could be acquired by establishing Z-scheme heterojunctions in photocatalysts. Also, under the circumstance of meeting the theoretical redox potentials of coinstantaneous CO2 reduction and H2O oxidation, we highlight that the photoabsorption of a semiconductor photocatalyst could be expanded into the IR light range by the introduction of an intermediate band, while we summarize that the IR light response could be achieved by virtue of the possessive partially occupied band of a conductor photocatalyst. Finally, we present a brief conclusion and an outlook concerning more potential strategies for sufficiently utilizing solar energy to realize CO2 photoreduction and wider application fields of broad-spectral-response photocatalysts.

### 2. Strategies for Realizing Visible-Light-Driven CO2 Reduction

As is well-known, the conventional wide-band-gap photocatalysts such as TiO2, ZnO, and ZrO2 normally have the abilities for coinstantaneous photocatalytic CO2 reduction and H2O oxidation thanks to their suitable CB and VB positions. However, their large band gaps unfortunately limit the solar energy utilization efficiency, which accounts for the low photocatalytic activities. In this case, many strategies have been developed to expand the photoabsorption of these wide-band-gap semiconductors from the UV light into the visible light range under the situation of maintaining their appropriate band edge positions, with effort to realizing the visible-light-driven CO2 reduction into valuable fuels.

#### 2.1. Visible-Light-Driven CO2 Reduction Realized by Narrow-Band-Gap Photocatalysts

Given this aspect, the narrow-band-gap semiconductors, possessing a visible light harvesting ability as well as proper CBs and VBs, may be the potential photocatalysts to realize visible-light-driven CO2 reduction (Figure 2A). To this end, Yu et al. have fabricated the Eosin Y-functionalized conjugated organic polymers (PEosinY-N, N = 1–3) through the Sonogashira–Hagihara cross-coupling process, in which the structural formulas for Eosin Y and aromatic alkenes of A1, A2, and A3 are shown in Figure 2B. As uncovered by the UV–vis spectra in Figure 2B, all the PEosinY-N photocatalysts displayed the visible light responses from 400 to 600 nm, while their band structures in Figure 2C implied their capacities for simultaneously realizing CO2 reduction and H2O oxidation. Benefiting from the narrow band gaps and the suitable CB and VB positions, all the PEosinY-N photocatalysts could achieve the photoreduction of CO2 into CO under visible light illumination (Figure 2D). Analogously, both the SnS2 atomic layers and CuIn5S8 single-unit-cell layers with befitting CB and VB positions as well as intense visible light absorption also exhibited the performances of CO2 reduction into CO under visible light irradiation.

As a result, developing more narrow-band-gap photocatalysts that possess strong visible light absorbance and well-matched band edge positions is the simplest and most effective strategy for realizing visible-light-driven CO2 reduction over a single photocatalyst without any sacrificial agent.
2.2. Visible-Light-Driven CO2 Reduction Induced by Defective Photocatalysts. To date, some works have affirmed that the narrow-band-gap photocatalysts could realize visible-light-driven CO2 reduction into carbon-based fuels, whereas the strict standard of appropriate CB and VB positions immensely limits the selection of narrow-band-gap photocatalysts. Recently, defect engineering has been considered as a vigorous approach for realizing visible-light-driven CO2 reduction. For instance, Shi et al. have demonstrated that the introduction of nitrogen defects in graphitic carbon nitride nanosheets could account for their expanded visible light absorption and hence realized visible-light-driven CO2 reduction.22 Also, Liu et al. have fabricated the oxygen-deficient TiO2 nanocrystals with different exposed facets, and all of them showed the increased visible light absorbance as compared to the corresponding perfect TiO2 nanocrystals, thus achieving a promoted performance of CO2 reduction under visible light irradiation.23 That is to say, as for the wide-band-gap photocatalyst with satisfied band edge positions for constantanxious CO2 reduction and H2O oxidation, introducing a new defect level within their CB and VB levels could expand its photosorption from the UV into the visible light region (Figure 3A). Given this, our group has created the oxygen vacancies on BiOBr atomic layers by continuous UV illumination for dozens of minutes. (C) Calculated density of states of oxygen-deficient BiOBr atomic layers. Reproduced with permission from ref 24. Copyright 2018 John Wiley & Sons, Inc.

For example, Wang et al. reported that introducing chromium (Cr) in mesoporous CeO2 (M-CeO2) photocatalysts resulted in the formation of a dopant energy level within the band gap of CeO2 (Figure 3D).27 Meanwhile, UV−vis spectra in Figure 3E showed that the presence of the dopant energy level enabled their visible light harvesting ability, thus exhibiting superior CO and CH4 formation rates for visible-light-driven CO2 reduction relative to the M-CeO2 photocatalysts. Consequently, the introduction of new levels in wide-band-gap semiconductors could extend the photosorption from the UV light to visible light region and hence realize visible-light-driven CO2 reduction.

2.3. Visible-Light-Driven CO2 Reduction Realized by Z-Scheme Heterojunction Photocatalysts. Based on the aforementioned analyses, it is still very challenging to construct single-component photocatalysts with broad-spectral response and appropriate band edge positions for CO2 photoreduction. Also, the single-component photocatalyst usually suffers from the low separation efficiency of electron−hole pairs, which causes damage on the photocatalytic performances. In this respect, a Z-scheme system constructed by two photocatalysts would help to concurrently address these two issues.28,29 Compared with the conventional heterojunctions, the Z-scheme ensures that the visible light−driven reaction can be better realized due to the expanded visible light absorption.30

Figure 2. (A) Schematic illustrating the band structures of narrow-band-gap semiconductors for CO2 photoreduction. (B) UV−vis spectra, (C) scheme of the band structures, and (D) CO and H2 yields for Eosin Y and PEosinY-N (N = 1−3). The inset in part B denotes the structural formulas for Eosin Y and aromatic alkyles of A1, A2, and A3. Reproduced with permission from ref 19.Copyright 2019 John Wiley & Sons, Inc.

Figure 3. (A) Schematic illustrating the band structures of wide-band-gap semiconductors with and without defects for CO2 photoreduction. (B) UV−vis spectra for BiOBr atomic layers after UV illumination (Figure 3C revealed that introducing oxygen vacancies in BiOBr atomic layers could lead to the generation of some new defect levels within the CB and VB levels, which accounted for the extended visible light absorbance and hence boosted the property of visible-light-induced CO2 reduction into CO. Similarly with the new defect levels aroused from defect engineering in photocatalysts, the extra energy levels produced by dopants in photocatalysts could also contribute to strengthening the visible light response of the photocatalysts.25,26 For example, Wang et al. reported that introducing chromium (Cr) in mesoporous CeO2 (M-CeO2) photocatalysts resulted in the formation of a dopant energy level within the band gap of CeO2 (Figure 3D).27 Meanwhile, UV−vis spectra in Figure 3E showed that the presence of the dopant energy level enabled their visible light harvesting ability, thus exhibiting superior CO and CH4 formation rates for visible-light-driven CO2 reduction relative to the M-CeO2 photocatalysts. Consequently, the introduction of new levels in wide-band-gap semiconductors could extend the photosorption from the UV light to visible light region and hence realize visible-light-driven CO2 reduction.

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have fabricated a Z-scheme g-C3N4/SnS2 photocatalyst that showed more excellent CH4 and CH3OH evolution rates than the single g-C3N4 or SnS2 photocatalyst,\(^3^2\) while Wang et al. have prepared a Z-Scheme α-Fe2O3/Cu2O heterostructure, which also achieved the property of CO2 reduction into CO under visible light irradiation.\(^3^3\) As a consequence, building a Z-scheme heterojunction in photocatalysts can not only contribute to obtaining more negative CB and positive VB positions for realizing visible-light-driven CO2 reduction but also enhance the carrier separation efficiency.

### 3. STRATEGIES FOR REALIZING IR-LIGHT-DRIVEN CO2 REDUCTION

Many researchers have already demonstrated that the photoresponse of a photocatalyst could be expanded from the UV light to visible light range for CO2 reduction,\(^3^4,3^5,3^6\) whereas the IR light that accounts for ca. 52% of the solar spectrum can not be effectively utilized. This is mainly attributed to the fact that IR-light-response photocatalysts normally possess extremely narrow band gaps, which gives rise to the inapposite CB or VB positions for cointaneous CO2 reduction and H2O oxidation.

#### 3.1. IR-Light-Driven CO2 Reduction Induced by Intermediate-Band Photocatalysts

To solve the unsurmountable contradiction between the effective utilization of IR light and the performance of CO2 reduction, introducing an intermediate band within the CB and VB of a semiconductor would be an efficient strategy for gaining the IR light absorbance under the guarantee of satisfying the theoretical redox potentials of CO2 reduction and H2O oxidation (Figure 5A). Taking the oxygen-defective WO3 atomic layers as an example,\(^3^7\) the density functional theory (DFT) calculations in Figure 5B disclosed that introducing a certain amount of oxygen vacancies can lead to the generation of an intermediate band in WO3 atomic layers. Also, the synchrotron radiation photoelectron spectroscopy (SRPES) valence-band spectra in

Figure 4. Schematic illustrating the band structures and charge transfer via (A) conventional mode and (B) Z-scheme mode in Cu2O/WO3-001 composites for CO2 photoreduction. (C) Transient photocurrent responses of the Cu2O, WO3-001, and Cu2O/WO3-001 Z-scheme composites, in which WO3-001 represents WO3 with dominant (0 0 1) facet. Reproduced with permission from ref 30. Copyright 2018 Elsevier. (D) Schematic illustrating the band structures and charge transfer in the ZnPc/BVNS Z-scheme photocatalyst for CO2 photoreduction, and (E) SPS spectra for 1ZnPc/BVNS and BVNS, in which 1 is the mass ratio of ZnPc to BiVO4. Reproduced with permission from ref 31. Copyright 2019 John Wiley & Sons, Inc.

Figure 5. (A) Schematic illustrating the band structure of the intermediate-band semiconductor for CO2 photoreduction, in which IB represents the intermediate band. (B) Calculated band structure for the oxygen-defective WO3 atomic layers slab, in which the concentration of oxygen vacancies is ca. 7.3%. (C) SRPES valence-band spectra, and (D) UV–vis spectra for Vc-rich WO3 atomic layers, Vc-poor WO3 atomic layers, and WO3 atomic layers. Reproduced with permission from ref 37. Copyright 2018 Elsevier.
unoccupied band (B1) could realize CO2 into CO under IR processes, in which the electrons generated in the lowest could undergo both the intraband and interband transition. This might be attributed to the fact that the CuS atomic layers were largely extended to visible light even to IR light with respect to the WO3 atomic layers. Benefiting from the efficient IR light harvesting caused by the defect-induced intermediate band, both the V_o-rich and V_o-poor WO3 atomic layers realized IR-light-driven CO2 reduction to CO, while the CO formation rate of the V_o-rich WO3 atomic layers was approximately 1.8 times higher than that of the V_o-poor WO3 atomic layers. Accordingly, the presence of intermediate bands induced by defect engineering in photocatalysts could help to extend the photoresponse into IR light region, thus effectively making use of IR light for CO2 photoreduction.

3.2. IR-Light-Driven CO2 Reduction Realized by Conductor Photocatalysts. Defective photocatalysts with intermediate bands have been attested to successfully realize the IR-light-driven CO2 reduction; however, the typical demerits of these semiconductors including sluggish carrier mobility and limited intrinsic carrier concentrations still lead them to suffer from the poor carrier transfer efficiency and the slow redox reaction kinetics. By contrast, conductor materials could be regarded as appealing photocatalysts thanks to their extra-high carrier concentrations and electric conductivity, which are approximately some orders of magnitude larger than those of the traditional semiconductors.38–40 More importantly, their near-zero band gaps endow their broad photoreponse expanding to IR light ranges, affording the prerequisite requirement for IR-light-driven CO2 reduction. Furthermore, compared with the semiconductors, the crucial partially occupied band in conductors also enables a transition process to generate plentiful charge carriers to participate in CO2 photoreduction. As exhibited in Figure 6A, the transition process mediated by the partially occupied band, such as the individual transition process (I and II) and the sequential transition process (III and IV), can not only ensure the IR light response but also endow the suited band edge positions for coistantaneous CO2 reduction and H2O oxidation.41 To this end, our group has fabricated the metallic CuS atomic layers, whose metallic nature could be verified by the incremental electrical resistance accompanied by increasing temperatures (Figure 6B), while their strong IR light response was confirmed by UV–vis spectra in Figure 6C. Actually, the CuS atomic layers realized IR-light-induced CO2 reduction into CO with an evolution rate of 14.5 μmol g−1 h−1, whereas the CuS bulk did not show any IR-light-driven CO2 activity. This might be attributed to the fact that the CuS atomic layers could undergo both the intraband and interband transition processes, in which the electrons generated in the lowest unoccupied band (B1) could realize CO2 into CO under IR light illumination, whereas the CuS bulk cannot acquire the interband transition from the Fermi level in the CB to B1 band owing to their large band gap. To further pursue other conductor photocatalysts for realizing IR-light-driven CO2 reduction, our group also synthesized the metallic CoN atomic layers, whose metallic character was affirmed by the incremental electrical resistance accompanied by increasing temperatures and the density of states crossed Fermi level in Figure 6D. Moreover, the UV–vis spectra in Figure 6E showed their effective IR light harvesting, and hence, the CoN atomic layers also achieved the performance of CO2 reduction into CO under IR light irradiation. On the basis of the above analyses, the IR-light-response conductors are the potential candidates for CO2 photoreduction.

4. CONCLUSION AND OUTLOOK

In this Outlook, we summarize the strategies for realizing visible-light- and IR-light-driven CO2 photoreduction over broad-spectral-response photocatalysts in aqueous solutions/H2O vapors without using any sacrificial agent. For instance, we describe that the narrow-band-gap PEosinY-N photocatalysts with befitting CB and VB positions realize CO2 reduction into CO under visible light irradiation. Also, we outline that the defect levels induced by oxygen defects in BiOBr atomic layers and the dopant energy levels caused by Cr dopants in M-CeO2 photocatalysts expand their photoreponses from the UV light into visible light region and hence achieve visible-light-driven CO2 reduction. Then, we see that more negative CB and positive VB positions for simultaneous CO2 reduction and H2O oxidation as well as the accelerated charge carrier separation efficiency are acquired by the establishments of Cu2O/WO3 and ZnPc/BVNS Z-scheme systems, which helps to enhance the photocatalytic CO2 performance under visible light irradiation. Moreover,
under the guarantee of satisfied standard potentials for CO₂ reduction and H₂O oxidation, we also review that the intermediate band induced by oxygen defects in WO₃ atomic layers leads to the expansive photoabsorption of IR light, thus realizing IR-light-driven CO₂ reduction; meanwhile, we highlight that the partially occupied band in the conductor photocatalyst of CuS atomic layers enables their strong IR light harvesting and hence realize the property of CO₂ reduction into CO under IR light illumination.

We summarize the strategies for realizing visible-light- and IR-light-driven CO₂ photoreduction over broad-spectral-response photocatalysts in aqueous solutions/H₂O vapors without using any sacrificial agent.

Although lots of enormous breakthroughs have been made in CO₂ photoreduction triggered by wide-spectral-response photocatalysts, there are still many strategies to be developed. For example, the integration of plasmonic metals (Au, Ag, Cu, etc.) with the wide-band-gap semiconductors may be an effective strategy for realizing visible-light- and even IR-light-driven CO₂ reduction. This is mainly ascribed to the fact that the hot-electron-injection effect caused by localized surface plasmon resonance (LSPR) could lead to the transfer of electrons from the Fermi level in plasmonic metals to the CB of the semiconductors, thus extending their absorption spectrum range. It is also worth expecting to combine the LSPR effect with the multiple light scattering and reflecting effect in photocatalysts, which helps to increase the efficient optical path-length of a photon and the possibility of photoabsorption and hence boost the visible-light- and IR-light-driven CO₂ reduction. Moreover, the upconversion nanomaterials, constructed by introducing some particular ions such as Ln³⁺, Er³⁺, Yb³⁺, and Tm³⁺ ions into the wide-band-gap photocatalysts, may sufficiently make use of the IR light for CO₂ reduction. That is to say, these particular ions could absorb the IR light and then emit the UV or visible light to excite the wide-band-gap photocatalysts to generate reductive electrons for CO₂ reduction. Furthermore, it is indispensable to deeply probe the internal mechanism for the transition of photoexcited carriers by means of advanced characterization technologies, which contributes to developing more new approaches for achieving the extended photoreponse of photocatalysts. In this respect, the ultrafast transient absorption spectroscopy could be employed to explore the charge-carrier dynamics, which is closely related to the photoabsorption and the band edge positions of photocatalysts. More importantly, the theoretical prediction of wide-spectral-response photocatalysts with appropriate band edge positions for CO₂ photoreduction still remains in the infancy stage. In this case, the machine learning technique would be a powerful tool to predict the CB and VB positions as well as the light absorption capacity of photocatalysts through regulating the calculation conditions and parameters. With the help of the machine learning technique, one can highly efficiently choose the potential wide-spectral-response photocatalysts to realize CO₂ photoreduction. Accordingly, it is believed that more wide-spectral-response photocatalysts will be designed and fabricated for CO₂ reduction on the basis of some other novel and yet-to-be discovered principles in the future. Last but not least, the wide-spectral-response photocatalysts can not be just applied in the field of CO₂ photoreduction, but they can also be utilized to enhance the efficiencies of other photocatalytic systems including water splitting, pollutant degradation, nitrogen fixation, and molecular activation.

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Notes

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