Photocatalytic CO₂ reduction attracts substantial interests for the production of chemical fuels via solar energy conversion, but the activity, stability, and selectivity of products were severely determined by the efficiencies of light harvesting, charge migration, and surface reactions. Structural engineering is a promising tactic to address the aforementioned crucial factors for boosting CO₂ photoreduction. Herein, a timely and comprehensive review focusing on the recent advances in photocatalytic CO₂ conversion based on the design strategies over nano-/microstructure, crystalline and band structure, surface structure and interface structure is provided, which covers both the thermodynamic and kinetic challenges in CO₂ photoreduction process. The key parameters essential for tailoring the size, morphology, porosity, bandgap, surface, or interfacial properties of photocatalysts are emphasized toward the efficient and selective conversion of CO₂ into valuable chemicals. New trends and strategies in the structural design to meet the demands for prominent CO₂ photoreduction activity are also introduced. It is expected to furnish a comprehensive guideline for inside-and-out design of state-of-the-art photocatalysts with well-defined structures for CO₂ conversion.

1. Introduction

Global warming has become an increasingly serious environmental concern because of the excessive emission of carbon dioxide in human activities.[1–3] In addition to CO₂ capture technology for geological sequestration,[4–6] solar-driven CO₂ conversion into chemical fuels is promising, which not only reduces the amount of CO₂ in the atmosphere, but also achieves carbon-neutral cycling.[7–11] Inspired from photosynthesis in nature, the researchers have devoted themselves to the studies of photocatalytic CO₂ reduction by directly using solar energy.[12–17] The photocatalytic CO₂ reduction meets perfectly with the green chemistry concept and with the imperative challenges regarding highly efficient photocatalysts by specialized structures, including crystal structure, microstructure, junction structure, surface structure, etc.[16,18–20]

Figure 1 shows the increase in the number of published papers and citations in this field since 1992 (by WOS). The number of published articles associated with “Photocat* AND CO₂” and “Photocat* AND Structure” is 1174 and 2565, respectively. A 3 year average growth rate of 26% and 5% is observed in published articles associated with “Photocat* AND CO₂” and “Photocat* AND Structure,” respectively. Thus, the CO₂ photoreduction has received considerable attention. The number of citations for the references about “Photocat* AND CO₂” and “Photocat* AND Structure” has exponentially increased in the past 5 years (from 2014 to 2019), reaching 12,554 and 14,789 with the average growth rate is 12.7% and 36.7%, respectively. Especially, citations for the references on “Photocat* AND Structure” increased by 45.4% in 2018, in sharp contrast to a ~5% growth rate in published papers. It indicates that the structure engineering is increasingly important and essential, which becomes the crucial means for improving the photocatalytic performance of semiconductors.

Previously, a few review papers on the structural designs of photocatalysts toward CO₂ conversation have been published.[21–24] For example, Li and coworkers provided a unique insight into yolk–shell-nanostructured photocatalysts for heterogeneous photocatalytic reactions.[10] Bai et al. received attention in the facet engineering on materials for photocatalytic application.[13] Recently, Zhao et al. have summarized the recent advances in 2D-based materials for the solar-driven CO₂ reduction to hydrocarbons.[25] But it is still not far enough to expose the huge potential of structure engineering from inside-and-out in this growing research field. In particular, a comprehensive overview of structural engineering for semiconductor-based photocatalytic CO₂ reduction is highly desirable and anticipated, which may provide top-down and bottom-up strategies for developing high-efficiency photocatalysts.

Herein, we proposed a comprehensive review of semiconductor structure engineering for CO₂ photoreduction. First, the fundamentals, challenges, and photocatalyst development of
CO₂ photoreduction were introduced. Then, the photocatalysts for CO₂ reduction with diverse kinds of structures, including nano-/microstructure, crystalline and band structures, surface structure and interfacial structure, were highlighted and discussed in details. Furthermore, several new structure systems were summarized. Finally, the key challenges and outlook on the future direction in this field were proposed.

2. Overview of Photocatalysts for CO₂ Reduction

2.1. Thermodynamic and Kinetic Challenges

Carbon dioxide is a stable molecule, featuring the linear and non-polar nature of the molecule. [26,27] Despite development for many years, the conversion efficiency and product selectivity of CO₂ photoreduction in mild condition are still quite low. So far, energy conversion efficiency of solar-to-fuel is C25 1% under AM 1.5G, which is mainly attributed to the following reasons: [28–34]

1) CO₂ is one of the most chemically inert reactants. The breaking of C─O bonds needs to consume huge energy with appropriate catalysts. The Gibbs free energy changes (ΔG) of specific reactions are shown in Table 1.[35,36] A standard state is positive (ΔG > 0), and it means that these reactions are non-spontaneous. In addition, the standard enthalpy changes (ΔH > 0) are also shown in Table 1, in which the positive ΔH values show that these reaction processes are endothermic under a standard state. It is apparent that these multielectrons reduction reactions from CO₂ to CO or organic small molecules are thermodynamically uphill, which are difficult to occur at ambient temperature and pressure.[36,37] 2) During the CO₂ photoreduction process, CO₂/C0 as a product of single-electron transfer demands a negative equilibrium potential of C25 1.9 V versus normal hydrogen electrode (NHE).[27,38] This overpotential is too high to accomplish for most photocatalytic systems, whereas other products from multielectrons transfer with a lower overpotential are easy to be generated. The band structure of some typical photocatalysts and the standard reduction potentials in CO₂ reduction are shown in Figure 2.[12,39] In the CO₂ photoreduction process, it requires that the conduction band (CB) position of photocatalysts is above the standard reduction potential, and the valence band (VB) position of photocatalysts needs potentials below the standard oxidation potential to achieve photooxidation.

Table 1. Calculated thermodynamic parameters (ΔG, ΔH, and ΔS) of typical CO₂ conversion reactions. Reproduced with permission.[36] Copyright 2017, Elsevier.

| Product  | Net reaction | ΔG° [kJ mol⁻¹] | ΔH° [kJ mol⁻¹] | ΔS° [J mol⁻¹ K⁻¹] |
|----------|--------------|----------------|----------------|-------------------|
| Hydrogen | H₂O + H₂ → 0.5 O₂ | 237.17 | 285.83 | 163.30 |
| Carbon monoxide | CO₂ + H₂O → CO + H₂O + 0.5 O₂ | 257.38 | 283.01 | 86.55 |
| Formic acid | CO₂ + H₂ → HCOOH + 0.5 O₂ | 269.86 | 254.34 | −52.15 |
| Formaldehyde | CO₂ + H₂O → HCHO + O₂ | 528.94 | 570.74 | 140.25 |
| Methanol | CO₂ + 2H₂O → CH₃OH + 1.5O₂ | 701.87 | 725.97 | 80.85 |
| Ethanol | 2CO₂ + 3H₂O → C₂H₅OH + 3O₂ | 1325.56 | 1366.90 | 138.75 |
| Propanol | 3CO₂ + 4H₂O → C₃H₇OH + 4.5O₂ | 1962.94 | 2021.24 | 196.65 |
| Methane | CO₂ + 2H₂O → CH₄ + 2O₂ | 818.18 | 890.57 | 242.90 |
| Ethane | 2CO₂ + 3H₂O → C₂H₆ + 1.5O₂ | 1468.18 | 1560.51 | 309.80 |
| Ethylene | 2CO₂ + 2H₂O → C₂H₄ + 3O₂ | 1331.42 | 1411.08 | 267.30 |
In the absence of sacrificial agent, the VB position of photocatalysts should be more positive than 1.23 V (vs NHE, in pH = 7), and thus photoinduced holes can contribute to O₂ formation.

But some photocatalysts can hardly satisfy both the standard reduction and oxidation potentials requirement. Achieving trial CO₂ reduction in the presence of sacrificial reagents is a feasible way for these photocatalysts. For example, triethanolamine is usually used as an electron donor in aqueous or organic solvent systems for CO₂ reduction.

The conversions of CO₂ into valuable products, such as CH₄,[43–50] CH₃OH,[51–55] or HCOOH,[56–61] have been reported, but the yield and selectivity of these products still need to be improved.[62] As the most common product in gas system, CO formation just requires two protons and two electrons, whereas CH₄ formation needs eight protons and electrons and prefers to be produced on noble metal catalysts. HCOOH generation can usually be achieved by sulfides (e.g., ZnS) with suitable metal doping, such as Ni or Cd, in liquid systems, and this process needs the same number of protons and electrons as CO formation, but demanding a higher overpotential.[63] Other products are usually hard to be observed with a high activity and selectivity, because they are always thermodynamically uphill and consume different electrons or protons through multiple reactions.[64] In practice, photocatalytic CO₂ reduction is much more complex due to various competing reactions, such as H₂ evolution in aqueous system. Thus, the mechanisms in diverse solvent system were studied for pursuing a high yield of target products. The mechanisms of CO₂ photoreduction in both gas and liquid phases to obtain desired products are still challenging.

There are also many kinetic challenges in CO₂ photoreduction. Specifically, the photoreduction reaction of CO₂ over photocatalysts includes the following processes: 1) light harvesting and generation of electron–hole pairs; 2) charge separation and migration from bulk to the surface of the semiconductors accompanied by the recombination electrons and holes in the bulk and on the surface of photocatalysts; 3) the reaction of electrons with absorbed CO₂ (normally the holes take part in O₂ evolution reaction in the meantime) and desorption of products from the surface of photocatalyst.[65–67]

Therefore, light harvesting, charge separation, and surface reactions are the three crucial steps that play decisive roles in CO₂ photoreduction.

2.2. Development of Semiconductor Photocatalysts for CO₂ Reduction

High photocatalytic activity with desirable products, including CO, CH₄, CH₃OH, or HCOOH, is a persistent pursuit for exploration of high-performance photocatalysts CO₂ reductions.[68–70] In other words, the purposes of structural engineering for photocatalysts are to increase the conversion efficiency and to control the selectivity of products in the CO₂ photoreduction reaction.[16,71–73] Generally, there are three factors that can regulate the final products of photocatalytic CO₂ reduction. 1) Efficient photogenerated charge separation can realize high surface electron density, which can regulate the final products by promoting multielectron reduction process. 2) Photocatalytic CO₂ reduction as a multistep reaction, diverse active sites on the surface can greatly affect the products selectivity. For example, regulating surface structure can affect the rate-determining step or key intermediates during the surface reaction, and thus obtaining different final products. 3) A strong adsorption capability of CO₂ molecules usually allows a high catalytic activity, but desorption properties may determine the final products. A decent desorption ability of target products is a key factor for pursuing a high selectivity.

A timeline of typical photocatalysts and diverse strategies for CO₂ photoreduction are shown in Figure 3. Since the first case of p-type GaP photoanode material was reported in 1978, few new photocatalytic materials have been found during the first several decades. In 1997, a study on Pt-loaded ex-Ti-oxide/Y zeolite was reported, which realized CH₄ production with high selectivity.[74] It means that the final product is not only CO, but also CH₄, thus the product selectivity enters researcher’s vision. After 1 year, the photocatalyst of Pt on Ti-MCM-48 achieved the switch of final products from CH₃OH to CH₄.[75] Researchers found that depositing different types or sizes of metals on the surface of semiconductors has an effect on photocatalytic selectivity. Also, different products can be obtained by controlling surface structures, such as acid–base sites[76–78] and organic groups.[79,80] Since 2009, several new photocatalytic systems have been proposed gradually, including g-C₃N₄,[81–90] CdS,[90–99] BiOCl,[100–102] and BiOBr.[103] Synthetic strategies for various nano-/microstructure were also developed, such as quantum dots (QDs),[104–106] nanowires (NWs),[107–109] and
heterostructures. These vigorous developments have led to the improvement of the conversion rate of CO2 reaction and the selectivity of final products.

2.3. Influence of Structure on Photocatalytic Activity

In the photocatalytic process of CO2 photoreduction, the total quantum efficiency ($\eta$) is considered to be determined by light-harvesting efficiency ($\eta_1$), charge migration efficiency ($\eta_2$), and redox reaction (charge utilization) efficiency ($\eta_3$), as shown in Equation (1).

$$\eta = \eta_1 \times \eta_2 \times \eta_3$$

After the formation of photoexcited charge carriers, most of the photoexcited electrons and holes tend to be consumed via recombination before the completion of surface catalytic reactions (Figure 4). Because the recombination processes significantly decrease the quantum efficiency of CO2 photoreduction, the researchers have been trying their best to relieve the recombination rate and degree of electrons and holes. It is worth noting that the time scales for different charge movement behaviors is also different. The charge separation and transport process take place within $10^{-6}$ s, and the surface reaction is a process of $10^{-4}$ s. In contrast, the recombination of electrons and holes occurs from $10^{-12}$ to $10^{-3}$ s, and particularly the recombination in the bulk phase of photocatalysts (approximately several picoseconds) is much faster than other processes and it also tends to occur through the entire photocatalytic process.

As each of the aforementioned steps needs to be well optimized to achieve highly active and selective photocatalysts, various structural design methods have been developed for promoting the photocatalytic CO2 reduction performance, as briefly listed in the following: 1) Construction of nano-/microstructures strategies can control the morphology, size, and shape of materials, which have substantial advantages for enhancing CO2 photoreduction activity, such as shortening charge migration pathway, increasing reactive catalytic sites boosting charge separation as well as extending optical transmission
length.  

2) Doping and formation of solid solution are two main approaches to tailor the crystalline and band structures of photocatalysts. The alteration in atomic composition bonding and coordination may result in the changes of light absorption, band edge level, and charge separation. 

3) Diverse reactive sites can be introduced on the surface by adjusting exposing specific facet and facet junction. Reactive exposing facet with amount of unsaturated coordinated atoms can facilitate the catalytic reactions, and facet junction with coexposed anisotropic facets allows spatial separation of photo-generated electrons and holes. In addition, creating acid–base sites or vacancy and ionic modification on the surface are capable of promoting light absorption, charge separation, and CO_2 activation. 

4) Schottky junction and Z-scheme junction are typical and efficient heterojunctions that can well engineer the interface structure. In Schottky junction, electrons move from semiconductor to metal to obstruct backflow, resulting in a high charge transfer efficiency. In Z-scheme junction, the photogenerated charge carriers are efficiently separated through the interface between semiconductor and semiconductor or semiconductor–metal–semiconductor, and meanwhile the strong oxidative and reductive potentials were maintained. 

5) A series of new photocatalytic systems are developed for CO_2 photoreduction, such as metal organic frameworks (MOFs), covalent organic frameworks (COFs), semiconducting biohybrids systems, and single atom. These systems have different chemical affinities to CO_2 molecules, and thus may change the redox reaction pathways during CO_2 reduction process. Meanwhile, polarity enhancement and creation of spatially separated active sites as new strategies for enhancing charge separation and optimizing reactive catalytic sites attracts intense attention. 

3. Nano-/Microstructure Engineering

3.1. Dimension Regulation

With the development of photocatalysts, many nanostructures have been fabricated including 0D QDs, 1D structures (NWs), 1D nanorods, nanobelts, nanotubes, and nanofibers, 2D (nanoplates, nanosheets), and 3D hierarchical structures. These structures have received extensive attentions in CO2 photoreduction because of improved photorespective region, optimized charge transfer path, as well as ample active sites for CO2 or H2O adsorption. 

3.1.1. 0D Quantum Dots

QDs are aggregated tiny particles or nanocrystals with diameter smaller than 10 nm. Due to their small size, the quantum confinement effect becomes prominent, which can cause the change of band structure and relative properties in semiconductor. 

CsPbBr3 (CPB) QDs were developed to convert CO2 into solar fuels under AM 1.5G simulated illumination. As a specific feature in QDs, quenching the emission peak in photoluminescence (PL) spectra was observed in CPB (Figure 5a). CPB continually donated photogenerated electrons to CO2, which achieved a yield of 23.7 μmol g⁻¹ h⁻¹ in electron consumption for reduced products. Over 99.3% of generated electrons were consumed by the formation of CO and CH4, with the average rate of 4.1 and 1.9 μmol g⁻¹ h⁻¹, respectively. Further, CPB QDs were anchored on NHx-rich porous g-C3N4 nanosheets (PCN) by N–Br bonding. CPB QDs with a size of 10 nm are dispersed evenly on PCN (Figure 5b), because the lattice spacing of 0.58 nm is square with (110) planes of orthorhombic CPB. The 20 wt% CPB with PCN as the optimal ratio showed a CO yield of 149 μmol g⁻¹ h⁻¹, which was 15 and 3 times higher than pure CPB and PCN under visible-light irradiation, respectively. The unique interaction via N–Br bond caused improved charge separation and extended the lifetime of charge carriers between CPB and PCN.

In addition to the single semiconductor system, binary QDs systems were also developed for photocatalytic CO2 reduction.  

Lian et al. demonstrated that the combination of CuInS2/ZnS QDs as sensitizers with trimethylamine-functionalized iron tetraphenylporphyrin (FeTMA) for CO evolution under 450 nm light irradiation. The absorption peak is located at 420 nm originating from the QDs the size of 2.5 nm (red solid line in Figure 5c). The light absorption of QDs was clearly improved by combined with FeTMA (red dashed line). Furthermore, the FeTMA molecules tended to connect with QDs partially, because of observation of an extra absorption peak at 415 nm. The turnover number (TON) of binary photocatalysts was 450 for CO evolution after 30 h irradiation, with a selectivity of 99%. The sensitization efficiency of this system was over 11 times as large as the current record for Fe–porphyrin system. This enhancement efficiency was inferred from the formation of active superstructures that each FeTMA can collect photoelectrons from surrounding QDs (inset of Figure 5c). Moreover, Li et al. reported that CQDs/Cu2O composites achieved a high photocatalytic CO2 reduction activity for yielding MeOH (55.7 μmol g⁻¹ h⁻¹) under visible light. From the high-resolution transmission electron microscopy (HRTEM) images of the carbon QDs (CQDs)/Cu2O composite, it can be seen that the 5 nm CQDs were deposited on the surface of Cu2O particles, and the lattice fringes of 0.25 and 0.32 nm correspond to the (111) planes of Cu2O and (002) planes of carbon, respectively (Figure 5d). The excellent performance of CQDs/Cu2O was caused by benign light absorption, and high charge separation and transfer efficiencies. Once Cu2O was excited by visible light, the electrons would be consumed for methanol evolution, and meanwhile the holes were transferred to the CQDs to generate O2 via H2O oxidation. 

Due to easily tuned surface states and good absorption of visible light, QDs as catalysts or cocatalysts show many advantages in CO2 conversion. They usually play a vital role in hybrid structures to realize increased redox active sites and promoted photoabsorption. In addition, QDs are much easier to bond with other components by electrostatic assembly than bulk photocatalysts.

3.1.2. 1D Nanorods, NWs, and Nanotubes

Constructing 1D nanorods or nanobelts usually expose active facets with large specific surface areas, which are beneficial to surface redox reactions. The morphology of 1D also leads
to a directional charge transfer pathway, and the small diameter of these photocatalysts allows a rapid transport of charge carriers from bulk phase to the surface (Figure 6a–c).

Kar et al.\textsuperscript{[211]} reported the preparation of square-shaped cross-sections \( \text{TiO}_2 \) nanorods by flame annealing method. The light absorption was extended to 620 nm with a dominant absorption peak at 450 nm. In addition, it was deduced that the long and ultrathin nanobelts probably have more active sites for CO\textsubscript{2} reduction reactions. As a result, a high CH\textsubscript{4} yield with a rate of 156.5 \( \mu \)mol g\textsuperscript{-1} h\textsuperscript{-1} was achieved over flame-annealed \( \text{TiO}_2 \) nanotubes in aqueous electrolyte (FANT\textsubscript{aq}). NWs are also promising substrates for constructing composite photocatalysts. Wang et al.\textsuperscript{[212]} reported the synthesis of large CuO NWs arrays (108 cm\textsuperscript{-2}) modified with ZnO nanoparticles (NPs) on their surface (Figure 6a), due to the epitaxial relationship of CuO (111) and ZnO (101). The fabricated composite photocatalysts had a feasible way to improve the activity for CO\textsubscript{2} photoreduction.\textsuperscript{[210]}

When the diameter of the NW is in the range of 1–100 nm, NW array structures tend to represent many interesting optical or electrical properties.\textsuperscript{[109]} and these properties can be improved by elements doping and defects introducing. Alo Taibi et al.\textsuperscript{[213]} demonstrated that the Mg-doped InGaN/GaN NW arrays on Si substrate reduced CO\textsubscript{2} into different products under sunlight (Figure 7a). Pt NPs with the diameter of \( \approx \)2–3 were evenly distributed on the NWs, which were composed of GaN shell at the InGaN segments (Figure 7b,c). Mg-doped InGaN/GaN is p-type semiconductor, whereas Ge-doped InGaN/GaN is n-type semiconductor. The CO and CH\textsubscript{4} yield of p-type InGaN/GaN NW arrays were 5 and 0.86 mmol g\textsuperscript{-1} h\textsuperscript{-1}, much higher than that of undoped NW arrays (0.4 and 0.18 mmol g\textsuperscript{-1} h\textsuperscript{-1}), respectively. The CO and CH\textsubscript{4} production rates of n-type InGaN/GaN NW arrays were just 0.09 and 0.08 mmol g\textsuperscript{-1} h\textsuperscript{-1}, separately. In addition, a high CH\textsubscript{3}OH evolution rate of 0.5 mmol g\textsuperscript{-1} h\textsuperscript{-1} was observed only for the p-type InGaN/GaN NWs (Figure 7d,e). The CO production rate of Mg-doped NW arrays was over 50 times higher than Ge-doped NW arrays, because Mg doping enhanced their lifetimes by three times. Once the electrons were transferred from CuO NWs to ZnO islands, they would be trapped by the defects on ZnO and took a longer time to be recombined.
decreased the surface potential barrier of InGaN/GaN to promote the adsorption and activation of CO₂.

Combining a surface plasmon resonance with NW array structures can promote both light harvesting and transfer of charge carriers in the semiconductors. Cu₂O nanorod arrays were modified by graphene and Au–Cu nanoalloys (3D Au–Cu/graphene/Cu₂O) for CO₂ reduction into CH₃OH (Figure 6d). The transfer pathway of photogenerated electrons in this system was proposed. After the capture of photons by Cu₂O to produce electrons and holes, electrons were transferred to the graphene layer and further moved to the Au–Cu particles. Thus, the CH₃OH yield of 3D Au–Cu/graphene/Cu₂O system (18.80 ppm cm⁻² h⁻¹) is more than six times higher than that of pristine 3D Cu₂O (2.42 ppm cm⁻² h⁻¹). AlOtaibi et al. reported the preparation of gallium nitride NW arrays (GaN NWs) on silicon (Figure 6e), which were able to reduce CO₂ into CH₄ and CO under UV–vis irradiation. The CH₄ yield of GaN NWs with Rh/Cr₂O₃ cocatalyst was increased to ≈3.5 μmol g⁻¹ h⁻¹ in 24 h, and the CH₄ evolution was further increased to ≈14.8 μmol g⁻¹ h⁻¹ by Pt NPs modification (Figure 6f).
In addition, by assembling the NW arrays into 3D architectures, such as branched superstructures, the activity of CO2 photoreduction could be favorably enhanced.

### 3.1.3. 2D Ultrathin Nanosheets

Recent studies demonstrated that 2D nanosheets have abundant reactive sites, which are in favor of reactants’ diffusion and products’ desorption for enhancing photocatalytic activity. Meanwhile, some specific products in CO2 photoreduction can easily desorb from the surfaces of certain nanosheets, resulting in a high selectivity in reaction.[215–217] A large variety of monocompontent and multicomponent hybrid nanosheets were prepared to maximize these advantages in CO2 reduction.

The SAPO-5 (a classic molecular sieve) nanosheets were fabricated with a thickness of about 3.0 nm.[218] The active sites was increased on the nanosheets, and the ultrathin geometry of the nanosheets promotes the diffusion of CO2 and H2O and desorption of the products. It was also found that the excited state existed in a long-time scale on the nanosheets, contributing to high photocatalytic activity. Thus, the ultrathin SAPO-5 nanosheets showed about 6 times as high CH4 evolution as SAPO-5 microrods. To take advantage of the complementary features of several kinds of nanosheets, composite nanosheets have been developed to improve charge dynamics and visible-light harvesting. The composite photocatalyst consisting of TiO2 and carbon nitride nanosheets (CNNS) was synthesized for CO2 reduction to CO.[219] TiO2/CNNS heterostructures with {001} exposing facets of TiO2 led to an increased CO2 adsorption capacity and enhanced charge transfer. The TiO2/CNNS heterostructure photocatalyst showed a high CO production rate, which ≈10 times as high as commercial TiO2 as benchmark photocatalyst (P25). In addition, the well-designed heterojunction 2D-ZnV2O6/pCN was constructed with intimate interfacial contact. In a liquid media, CH3OH production rate of 2D-ZnV2O6/pCN (3742 μmol g⁻¹) was 1.15 and 5 times as much as that of the pure ZnV2O6 (3254 μmol g⁻¹) and protonated g-CN (753 μmol g⁻¹) within 4 h, respectively. In gas phase system, the CO was the dominant product of 2D-ZnV2O6/pCN nanosheets with a yield of 3237 μmol g⁻¹ after 4 h.

With the decrease in thickness, large number of unsaturated atoms emerged on the surface and edges, which endow 2D ultrathin materials with sufficient active sites for molecules adsorption and subsequently redox reactions.[220–223] The BiOBr atomic layers were fabricated to optimize CO2 reduction processes. The average thickness of BiOBr nanosheets is about 0.81 nm, which is equal to the thickness of single-unit-cell along [001] direction (Figure 8a–c). Single-unit-layer BiOBr contained abundant oxygen vacancy (OV), which enabled the photoabsorption in visible region and trapped electrons to activate CO2 molecules for producing COOH⁻ intermediate (Figure 8d–g). Therefore, BiOBr atomic layers demonstrated a greatly enhanced CO2 reduction activity, and the CO evolution rate (87.4 μmol g⁻¹ h⁻¹) is 24 times as high as that of bulk BiOBr. Han et al. reported the synthesis of three-unit-cells single-crystal InVO4 nanosheets, which is ≈1.5 nm in thickness[224] (Figure 8h–i). The surface photovoltage (SPV) response of InVO4 ultrathin sheet (30–60 mV) is much

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Figure 7. a) A 45 °C tilted scanning electron microscope image of p-InGaN/GaN NWs grown on a Si(111) substrate, and schematic of a p-InGaN/GaN NW photocatalyst decorated with Pt NPs inset in (a). b) Top: STEM-HAADF image of the pInGaN/GaN NW structure. Bottom: Pt map extracted from the selected region marked in red in (b, top) displayed in pseudocolor scale. c) Top: elemental Ga map from the selected region marked in green from (b, top). Bottom: thickness-projected in content map obtained from the selected region marked in green in (b, top). The x in InₓGa₁₋ₓN is presented in the color scale shown on the left. d) Measured CO, CH₄, and CH₃OH evolution rates on Pt-decorated p-InGaN/GaN NW photocatalysts under the full spectrum of a Xe lamp equipped with an AM1.5G filter. e) CH₃OH evolution over Pt-decorated p-InGaN/GaN NWs as a function of time under visible-light illumination (>400 nm). The inset shows CO and CH₄ generation rates on Pt-decorated NWs. Adapted with permission.[213] Copyright 2016, American Chemical Society.
higher than that of pristine InVO₄ (0–10 mV) under light illumination (Figure 8k–m), indicating that the ultrathin nanosheets substantially depressed the recombination of electrons and holes. CO as the main product can easily desorb from the {110} surface of InVO₄ ultrathin sheets in the photoreduction process, which resulted in a 6-times increase in CO generation rate (18.28 μmol g⁻¹ h⁻¹) compared with the nanocube counterpart (3.21 μmol g⁻¹ h⁻¹). In addition, ultrathin CoSe₂ with abundant Co vacancies was also developed by exfoliating CoSe₂ precursor by Xie and coworkers (Figure 9a,b).[225]

A large-scale synthesis of ultrathin nanosheets with desirable defects is a great challenge. The gram-scale single-unit-cell vanadium(V)-defective orthorhombic-BiVO₄ layers (Vᵥ-rich o-BiVO₄) was achieved by Xie and coworkers (Figure 9c,d).[226] SPV measurement demonstrated that V vacancies induced the photogenerated electrons to move toward the surface, while the holes were transferred to the bulk of Vᵥ-rich o-BiVO₄ (Figure 9e). Abundant V vacancy increased the lifetime of photogenerated carriers from 74.5 to 143.6 ns (Figure 9f,g). As a result, Vᵥ-rich o-BiVO₄ exhibited a high CH₃OH formation rate up to 398.3 μmol g⁻¹ h⁻¹ and an apparent quantum efficiency (AQE) of 5.96% at 350 nm, far exceeding that of Vᵥ-poor o-BiVO₄ (Figure 9h).

2D ultrathin nanosheets have ample unsaturated atoms as the defective sites, which are capable of promoting the light absorption, charge separation, and reactants adsorption. Although a number of 2D photocatalysts has been developed for CO₂ reduction, there is still a great difficulty to the synthesis of ultrathin nanosheets on the large scale. Especially, the controllable synthesis of 2D ultrathin photocatalysts with adjustable thickness is also challenging.

### 3.1.4. 3D Hierarchical Structure

Photocatalysts with 3D structure, such as nanosheets-assembled flowers,[227–233] hollow spheres,[234–243] and hierarchical NW
arrays, have been widely developed. Due to their special features, including high specific surface area and high light utilization, they always demonstrate excellent photocatalytic CO₂ reduction performance.

Wang et al. reported the preparation of marigold-like SiC@MoS₂ nanoflower (Figure 10a–d). The high electron mobility allows an efficient multielectronic reduction reaction on the surface of SiC, resulting in CH₄ as a main reduction product. The overall conversion of CO₂ with H₂O was achieved with the CH₄ and O₂ evolution rates of 323 and 621 μL g⁻¹ h⁻¹ in 40 h without sacrificial reagents under visible-light irradiation (λ ≥ 420 nm), respectively. In addition, SiC@MoS₂ also showed high stability during the CO₂ reduction reaction, because of the high chemical stability of MoS₂ nanosheets on SiC surface. In addition, Wang et al. demonstrated the fabrication of In₂S₃–CdIn₂S₄ heterostructure nanotubes for visible-light-driven CO₂ reduction (Figure 10e–i). Due to the nanosized interfacial contacts and unique microstructure, these hierarchical nanotubes showed many advantages, like enhanced charge separation and exposed rich active sites for CO₂ adsorption. The In₂S₃–CdIn₂S₄ nanotubes showed high CO generation rate with a rate of 825 μmol h⁻¹ g⁻¹ under visible-light irradiation without cocatalysts.

In addition to the high specific surface area and rich reactive sites for adsorption, the 3D NWs array with desirable configuration have the benefits of promoted light harvesting and charge separation. Kim et al. developed a ternary composite photocatalyst composed of Cu₃O NW arrays, carbon layers, and BiVO₄ NPs for photocatalytic CO₂ conversion (Figure 11a).
The BiVO$_4$/carbon-coated Cu$_2$O NW arrays (BVO/C/Cu$_2$O NWAs) showed irregular and rough surfaces with a diameter of $\approx 40$ nm and length of a few micrometers (Figure 11b,c). It exhibited significantly enhanced electrochemical capacitance of 3D Cu$_2$O NWAs (88.75 mF cm$^{-2}$), which is 3.57 times as high as that of Cu$_2$O on mesh (24.87 mF cm$^{-2}$) (Figure 11d). Under visible-light irradiation, CO formation rate of BVO/C/Cu$_2$O NWAs was 9.4 and 4.7 times as high as that of Cu$_2$O mesh and Cu$_2$O NWAs, respectively (Figure 11e). Moreover, BVO/C/Cu$_2$O NWAs showed advantages for multielectrons CO$_2$ reduction reactions. Specifically, CH$_4$ formation was only observed for BVO/C/Cu$_2$O NWAs (Figure 11f), in view of that CH$_4$ production is an eight-electron transfer reaction, much complex than CO formation (two-electron transfer reaction). Therefore, the construction of hierarchical nanostructures has proven to be effective strategies for photocatalytic CO$_2$ reduction. The nano-/microstructured photocatalysts with different dimensions for CO$_2$ reduction are shown in Table 2.

### 3.2. Porous Structure

Building a porous structure is a practicable strategy for enhancement of the photocatalytic performance. Microporous (pore diameters of less than 2 nm), mesoporous (pore diameters...
between 2 and 50 nm in Figure 12a–c), and macroporous (pore diameters of greater than 50 nm) materials have been demonstrated to promote CO$_2$ adsorption, increase reactive sites, and enhance light absorption.[259] It was also reported that mesopores not only enhanced the light absorption, but also facilitated the charge separation and migration of semiconductors.[260] For example, the ordered mesopores extended the photoresponse of TiO$_2$ from UV to visible region (Figure 12d,e).[261] To explore detailed parameters in porous structure, porosity properties are usually characterized by nitrogen sorption isotherm analysis(Figure 12f,g).[262]

A series of ordered mesoporous materials with high specific surface area (over 100 m$^2$ g$^{-1}$), including TiO$_2$, SnO$_2$, ZnS, ZnSe, CdS, and CdSe, were synthesized for converting CO$_2$ into CO or CH$_4$ under light irradiation.[263] The CH$_4$ yield of mesoporous TiO$_2$ and SnO$_2$ was $\approx$10 times as much as that of P25, which is attributed to their high specific surface area. Mesoporous ZnS showed the highest CH$_4$ production rate of 3.620 μmol g$^{-1}$ h$^{-1}$, while mesoporous CdSe showed the largest CO yield of 5.884 μmol g$^{-1}$ h$^{-1}$ (Figure 12h,i). Tailoring the porosity of photocatalysts is effective to improve the photocatalytic CO$_2$ reduction activity.[264] Feng et al.[265] first prepared

![Figure 11. Morphology of BVO/C/Cu$_2$O NWs: a) Schematic of the synthesis of BVO/C/Cu$_2$O NWAs. b) Large-area SEM image and c) SEM image with inset showing the optical image of BVO/C/Cu$_2$O NWAs; d) high-resolution TEM image of a BVO/C/Cu$_2$O NW. And photocatalytic CO$_2$ reduction of the various catalysts: e) CO formation rate and f) CH$_4$ formation rate for each composite. Adapted with permission.[258] Copyright 2018, American Chemical Society.](www.advancedsciencenews.com)
Table 2. The nano-/microstructured photocatalysts with different dimensions for CO2 reduction.

| Photocatalyst | Morphological features | Products | Yield | Reaction conditions | Ref. |
|---------------|------------------------|----------|-------|---------------------|------|
| CsPbBr3 perovskite QDs on porous g-C3N4 | \ | CO | 149 μmol g⁻¹ h⁻¹ | Visible light | [207] |
| CuInS2/ZnS QDs | Particle diameter of 2.5 nm | CO | TON = 124 ± 5 | 450 nm light | [182] |
| Rh/Cr2O3 decorated GaN NWs | Rh/Cr2O3 core/shell nanostructures on GaN NWs with an average diameter of ~3 nm | CH₄ | 3.5 μmol g⁻¹ h⁻¹ | 300 W xenon lamp | [214] |
| Carbon-decorated cuprous oxide mesoporous nanorods | The nanorod composed of NPs with a diameter of about 20 nm | CH₄ | AQEs: 0.71% | 350 W xenon lamp with 420 nm cut off filter | [266] |
| Rh/Cr2O3 decorated GaN NWs | Rh/Cr2O3 core/shell nanostructures on GaN NWs with an average diameter of ~3 nm | CH₄ | 5 μmol g⁻¹ h⁻¹ | | |
| Mg-doped Ga(In)N NWs | Diameter of ≈100–120 nm and length of ≈600–800 nm. | CH₃OH | 0.5 μmol g⁻¹ h⁻¹ | Full spectrum of Xe lamp with an AM1.5G filter | [213] |
| CuO NWs with ZnO islands | Diameter of 230 nm and length of 1.2 μm | CO | 1.98 mmol g⁻¹ h⁻¹ | 400 W Xe lamp | [212] |
| Zinc silicate nanosheets | Ultrathin nanosheets morphology with thicknesses of 8–15 nm and lateral size of about 200 nm | CO | 126.7 μmol g⁻¹ h⁻¹ | Simulated sunlight | [112] |
| CuO-decorated WO₃ nanosheets with dominant {001} facets | – | CO | 5.7 μmol g⁻¹ h⁻¹ | 300 W Xenon arc lamp with 420 nm filter | [391] |
| C₃N₄ nanosheets and a binuclear ruthenium(II) complex | – | HCOOH | TON > 2000 | Visible light with 420 nm filter | [336] |
| {001} facet-dominated TiO₂ nanosheets modified with sulfuric acid | Uniform sheet-shaped truncated octahedral bipyramid structures with an average thickness of 41 nm and a side length of 120 nm. | CH₄ | 3.3 μmol g⁻¹ h⁻¹ | 500 W Xe lamp with 420 nm filter | [328] |
| Carbon-doped BN nanosheets | Overall thickness of around 3–4 nm. | CO | 93 μmol g⁻¹ h⁻¹ | 300 W Xe lamp with 420 nm filter | [282] |
| Defect-rich ultrathin ZnAl-LDH nanosheets | The thickness of 40 nm | H₂ | 28 μmol g⁻¹ h⁻¹ | | |
| TiO₂/CNNS nanosheets | Average particle size of 15 nm | CO | 2 μmol g⁻¹ h⁻¹ | 150 W Xe lamp with 325 nm filter | [219] |
| SAPO-5 ultrathin nanosheets | The thickness of 3 nm | CH₃OH | 208.8 μmol g⁻¹ h⁻¹ | 254 nm UV light | [218] |
| ZnV₂O₆/g-C₃N₄ | – | CH₃OH | 3742 μmol g⁻¹ h⁻¹ | 35 W high-intensity discharge | [478] |
| 2D/2D nanosheets heterojunction | | | | | |
| SiC hollow spheres | The size of SiC hollow microspheres of about 10 μm | CH₄ | 16.8 μmol g⁻¹ h⁻¹ | 300 W Xe lamp | [479] |
| Photocatalyst | Morphological features | Products | Yield | Reaction conditions | Ref. |
|--------------|------------------------|----------|-------|---------------------|-----|
| AuPd/3DOM-TiO₂ (3DOM indicates 3D-ordered microporous) | The diameters of periodic voids in the range of 200 ± 10 nm, sublayer pores with relatively small sizes (60 ± 10 nm) | CH₄ | 18.5 μmol g⁻¹ h⁻¹ | 300 W Xe lamp (320–780 nm) | [480] |
| g-C₃N₄ nanotubes with decorated transparent ZIF-8 nanoclusters | Diameters of 0.5–3 m and lengths of several tens to hundreds of micrometers | CH₃OH | 0.75 μmol g⁻¹ h⁻¹ | 300 W Xe arc lamp | [81] |
| Core–shell-structured photocatalysts of Pt/TiO₂ nanocrystals wrapped by rGO | The average particle size of TiO₂ nanocrystals of 30 nm | CH₄ | 41.3 μmol g⁻¹ h⁻¹ | 300 W Xe lamp (320–780 nm) | [481] |
| 3D porous g-C₃N₄/C nanosheets | Graphene-like lamellar structure with the thickness of about 4 nm | CO | 32.7 μmol g⁻¹ h⁻¹ | Xe arc lamp (500 W) | [269] |
| Hollow heterostructured g-C₃N₄/CeO₂ with rich oxygen vacancies | Nanopores with average sizes of 300 nm to 400 nm and shell thickness of about 70 nm | CH₄ | 0.88 μmol g⁻¹ h⁻¹ | Xe lamp with 420 nm filter | [482] |
| 3D porous g-C₃N₄/graphene oxide aerogel | Adjustable macropore size from 147 ± 25 to 232 ± 32 nm, 289.2 m² g⁻¹ | CO | 3.83 μmol g⁻¹ h⁻¹ | 500 W Xe lamp with 420 nm filter | [483] |
| Hierarchical CuO–TiO₂ hollow microspheres | The microspheres of 1000 nm in diameter and the shell of 110 nm in thickness | CO | 14.54 μmol g⁻¹ h⁻¹ | Hg UV lamp (40 W, 254 nm) | [198] |
| TiO₂ microspheres with hierarchical nanostructure | TiO₂ spheres of 1.3 μm in diameter and on the outer surface mesopores (voids) in the range from 10 to 50 nm, 50.2 m² g⁻¹ | CH₄ | 0.9 μmol g⁻¹ h⁻¹ | Hg UV lamp (40 W, 254 nm) | [195] |
| Hierarchical In₂S₃-CdIn₂S₄ heterostructured nanotubes | The MIL-68 hexagonal prisms of about 9 μm in length, and 500 nm in diameter, the In₂S₃ nanotubes with shell thickness of about 100 nm | CO | 825 μmol g⁻¹ h⁻¹ | 300 W Xe lamp with a 400 nm cutoff filter | [191] |
porous TiO2 by pyrolyzing MIL-125, and coated MgO overlayer on porous TiO2. Porous TiO2 with five layers of MgO showed the optimal photocatalytic activity with a CO production rate of 13.5 μmol g−1 h−1, which is 21 times as high as that of P25. The coating of MgO on TiO2 reduced the recombination of photogenerated electrons and holes on the surface of TiO2. Similarly, mesoporous Cu2O covered by carbon layer realized the C2H4 evolution from CO2 reduction.[266] The thin carbon layer solved the photocorrosion of Cu2O, and the building of the mesoporous nanostructure promoted the adsorption of reactant molecules (Figure 12j,k) and charge carrier transfer. The optimized sample (C-2/Cu2O) showed an AQE of 2.07% for CH4 and C2H4 at λ = 400 nm under visible light (Figure 12l,m).

To develop composite structures with wide-ranging pore dimensions, metals or metal oxides were loaded into the mesoporous silica. These new active sites introduced by heteroatoms led to improved adsorption of CO2 for photoreduction. Tasbihi et al.[267] prepared Pt/TiO2-ordered mesoporous silica (TiO2-COK-12) for photocatalytic CH4 and CO evolution. Under UV light in a continuous flow gas-phase photoreactor, CO was the major final product catalyzed by TiO2-COK-12. Because Pt as a cocatalyst was favorable for CH4 formation as final product, loading the Pt/TiO2 catalysts on COK-12 improved the activity of CH4 with a selectivity of 100% in the reaction. Li and coworkers[268] synthesized mesoporous silica-supported Cu2O/TiO2 nanocomposites for CO2 photoreduction to CO and CH4. The large specific surface area of mesoporous silica (>300 m2 g−1) not only greatly promoted CO2 photoreduction and TiO2 dispersion, but also realized the more feasible adsorption of reactants. In blank TiO2–SiO2 system without Cu2O, CO was the primary product generated from CO2. The overall CO2 conversion efficiency and the selectivity for CH4 production were markedly increased by adding Cu2O. Cu species as an addition enhanced multielectrons reactions and suppressed the recombination of electrons and holes. Thus, 0.5%Cu/TiO2–SiO2 displayed the peak production rates of CO and CH4 reached 60 and 10 μmol g−1 h−1, respectively. Heteroatom loading, immobilizing redox sites and tailoring hierarchical nanostructure have been also utilized for designing porous g-C3N4-based photocatalysts. The g-C3N4 with a porous structure can facilitate the diffusion of CO2 towards redox active sites. Wang et al.[269] prepared the 3D porous g-C3N4/C nanosheets composites, which achieved prominent CO2 reduction. The CO and CH4 yields were 229 and 112 μmol g−1 under

Figure 12. Mesoporous single-crystal (MSC) synthesis of TiO2. a) Replication of the mesoscale pore structure within the templated region (FFT inset, 43 ± 3 nm sixfold symmetry) with crystal lattice vectors implied from the particle symmetry overlaid (reaction conditions 170 °C, 40 mM TiF4). b,c) Fully mesoporous TiO2 crystals grown by seeded nucleation in the bulk of the silica template. Adapted with permission.[265] Copyright 2013, Nature Research. Representative TEM images along d) (100) and e) (110) planes of the ordered mesoporous black TiO2 materials after hydrogen gas annealing at 500 °C. Adapted with permission.[261] Copyright 2014, American Chemical Society. f) Nitrogen sorption isotherms of polymers at 77 K. For clarity, the isotherms of CPOP-30-Re, CPOP-30’-Re, CPOP-31, and CPOP-31-Re are shifted vertically by 300, 500, 600, and 1000 cm3 g−1, respectively. g) Pore size distribution profiles for polymers calculated by nonlocal density functional theory. Adapted with permission.[262] Copyright 2019, American Chemical Society. h) Yields of CH4 using various photocatalysts, P25 (commercial TiO2, Degussa, anatase + rutile phases) and mesoporous materials (TiO2, SnO2, CdS, CdSe, ZnS, and ZnSe). i) Yields of CO using various photocatalysts, P25 (commercial TiO2, Degussa, anatase, and rutile phases) and mesoporous materials (TiO2, SnO2, CdS, CdSe, ZnS, and ZnSe). Adapted with permission.[263] Copyright 2018, Elsevier. j) N2 adsorption–desorption isotherm curves, k) CO2 adsorption isotherm curves, for pure Cu2O and C-2/Cu2O. Time-dependent product evolution over l) pure Cu2O and m) C-2/Cu2O. Adapted with permission.[266] Copyright 2016, American Chemical Society.
7 h simulated solar irradiation, both yields over 25 times higher than that of bulk g-C3N4.

Constructing porous structures are widely used in CO2 photoreduction because of their excellent adsorption capability and abundant structural defects. Rationally tailoring the sharp and pore size of photocatalysts enables the remarkable improvement in light absorption and charge separation.\(^{[270–272]}\) The coupling of single atom with nanoscaled metal oxides, mesoporous silica\(^{[65]}\) or shape-controllable porous nanomaterials are appealing nanostructured photocatalysts for CO2 reduction.

4. Crystalline and Band Structures Engineering

At present, various modifications on crystalline structure by tuning the compositions of semiconductors, such as element doping, can also change the electronic band structure, which results in the amelioration of the crucial factors during the photocatalytic process, thereby promoting the enhancement of CO2 reduction performance.\(^{[273,274]}\) For instance, constructing ordered mesoporous structure allowed TiO2 improved light absorption, leading to enhanced photocatalytic CO2 reduction activity.\(^{[263]}\) and QD structure improved the charge separation efficiency of CsPbBr3.\(^{[206]}\) Other modifications can either increase the adsorption of CO2, or adjust the final reductive products, so that the selectivity of CO2 reduction can be controlled.

4.1. Heteroatom Doping

Doping is always accompanied by the presence of vacancy defects in the crystal structure, which is due to the imbalance of charge or coordination in bulk structure.\(^{[275–277]}\) The proper balance between doping and vacancies can extend visible-light absorption, reduce the charge recombination, and maintain the adsorption of CO2, thus contributing to the prominent performance for CO2 photoreduction. On the contrary, excessive doping amount will throw off and does not usually guarantee an increase in photocatalytic activities.\(^{[278,279]}\)

The doping of metallic atoms in photocatalysts is widely investigated. Pang et al. reported the monodispersed Ni-doped ZnS (ZnS: Ni) nanocrystals as excellent visible-light responsive photocatalysts for converting CO2 into HCOOH.\(^{[280]}\) The introduction of Ni resulted in the presence of sulfur vacancy, and proper concentration of doped Ni maintained the strong absorption and abundant sulfur vacancy, which can reduce the charge recombination in the bulk phase. Whereas, a heavy doping of Ni resulted in the diminishing of sulfur vacancies, losing active sites for CO2 reduction. It was disclosed that the 0.1% doping of Ni as optimized ratio kept a good balance between the capacity of light absorption and the amount of sulfur vacancy. Consequently, over 95% selectivity of HCOOH as product and quantum efficiency of 91.9% at 340 nm and 36.6% at 420 nm were observed over Ni (0.1%)-doped ZnS nanocrystals. In addition to single element doping, the dual-elements doping was also conducted. A series of Cu/Zn doped/TiO2 photocatalysts were developed for CH4 evolution from CO2 reduction.\(^{[281]}\) Due to the Cu/Zn doping, the bandgap energy was reduced from 3.25 to 2.95 eV, and a strong CO2 chemisorption was observed for 2%CuO–19% ZnO/TiO2, indicating the increased the amount of active sites.

2%CuO–19%ZnO/TiO2 hence displayed an increased CH4 production (184 mol g\(^{-1}\)) within 24 h irradiation, which is higher than TiO2 (128 mol g\(^{-1}\)) and 2%CuO/TiO2 (153 mol g\(^{-1}\)).

The nonmetal doping also plays an important role in ameliorating the crystalline and band structure, which usually improves the light absorption and charge separation efficiency, contributing to the enhanced photocatalytic activity of CO2 reduction. The boron carbon nitride (h-BCN) was explored for producing CO from CO2 under visible-light illumination (Figure 13a).\(^{[282]}\) In h-BCN structure, C was incorporated in the h-BN lattice, which affected the bonding energies B–K, N–K, and C–K (Figure 13b). The optical absorption edge of h-BCN showed obvious redshifts with the enriching of carbon (Figure 13c). Under visible-light irradiation for 2 h, the evolution of CO and H2 increased to 9.3 and 2.9 μmol, respectively. Similarly, a carbon-doped SnS2 (SnS2-C) nanostructured photocatalyst was synthesized by Shown et al.\(^{[283]}\) It showed a high activity for CO2 reduction into hydrocarbons with a quantum efficiency of over 0.7% under visible light. Because doped C induced microstrain in the SnS2 lattice (Figure 13d,e), the electronic band structures and optical properties were largely altered. The observed maximum cumulative acetaldehyde yields after 13 h was 1256.6 mmol g\(^{-1}\)) within 24 h irradiation, which is higher than that of pristine g-C3N4.\(^{[284]}\) The OCN-tubes were allowed a narrow bandgap for improved light harvesting, charge separation, and CO2 adsorption. Thus, the methanol evolution of OCN-tube was 0.88 μmol g\(^{-1}\) h\(^{-1}\), which is five times as high as that of bulk g-C3N4 (0.17 μmol g\(^{-1}\) h\(^{-1}\)). Similarly, g-C3N4 with sulfur doping also showed an increased methanol evolution rate of 1.12 μmol g\(^{-1}\) h\(^{-1}\), higher than that of pristine g-C3N4 (0.81 μmol g\(^{-1}\) h\(^{-1}\)).\(^{[285]}\) The S doping resulted in the formation of impurity state, which was beneficial to the transfer of photogenerated electrons to CB for CO2 reduction.

Elements are commonly doped into bulk structure either by replacing the lattice atoms or by occupying the interstitial sites. With optimizing the doping with diverse elements, high performance with different final products in CO2 reduction can be achieved. Various doping sites and concentrations are closely associated with the light absorption, charge carrier separation, and CO2 chemisorption, which is vital for high activity and selectivity of CO2 reduction. But it still remains to be a significant challenge in ensuring a balance between the proportion of doping element and vacancy defects in bulks.

4.2. Solid Solution

Introducing proper elements or components to construct solid solution semiconductors through precise and wide-range replacement are important route for crystalline structure regulation.\(^{[286]}\) Ions radius, chemical valence, and crystallographic parameters are basically three vital keys to design solid solution structure and to minimize formation energy. As the composition of semiconductors is associated with the band structure and
electron–hole mobility, the introduced elements or components can generally tune the band structure and optoelectronic properties of semiconductors, which effectively adjust bandgap, band edge levels, and transport of photogenerated charge carriers.\[287,288\]

Halogens are good candidates for composition regulation to form solid solution. Bai et al.\[289\] prepared Bi$_4$O$_5$Br$_x$I$_{2-x}$ (x = 0, 0.5, 1, 1.5, and 2) solid solution through the molecular precursor method. Most of the Bi$_4$O$_5$Br$_x$I$_{2-x}$ solid solution showed higher CO$_2$ reduction activity for producing CO and CH$_4$ than Bi$_4$O$_5$Br$_2$ and Bi$_2$O$_3$I$_2$, and the highest photocatalytic activity for CO$_2$ reduction was obtained for Bi$_4$O$_5$BrI (x = 1) with a CO production rate of 22.85 μmol h$^{-1}$ g$^{-1}$ and AQE of 0.372 at 400 nm.

Figure 13. a) Typical TEM dark-field image of BCN-30 sample and the elemental mapping images of B, C, and N of the enlargement of selected-area in the picture. Scale bar, 300 nm. b) EELS spectra of BCN-x sample, c) bandgap determination of the BCN-x samples. Adapted with permission.\[282\] Copyright 2015, Nature Research. d) High-resolution XPS Sn 3d spectra of SnS$_2$-C and SnS$_2$. e) High-resolution XPS S 2p spectra of SnS$_2$-C and SnS$_2$. Comparative photocatalytic CO$_2$ reduction activity of SnS$_2$-C and SnS$_2$. f) Cumulative acetaldehyde formation yield of SnS$_2$-C and SnS$_2$. g) Comparative solar fuel formation rate and quantum efficiency of SnS$_2$-C, SnS$_2$, and commercial SnS$_2$ under a visible-light source (300 W halogen lamp). Adapted with permission.\[283\] Copyright 2018, Nature Research.
It was uncovered that the largely enhanced photocatalytic performance of Bi$_2$O$_5$BrI was ascribed to its high CB position, the highest ability for capturing CO$_2$ molecules and highest photoinduced carrier separation efficiency compared with Bi$_2$O$_5$Br$_2$ and Bi$_2$O$_5$I$_2$. Similarly, Gao et al.\cite{290} reported the preparation of the nanostructured BiOBr$_x$Cl$_{1-x}$ solid solution (Figure 14a). The construction of BiOBr$_x$Cl$_{1-x}$ solid solution optimized the bandgap and facilitated the photogenerated charges separation. Under simulated solar light irradiation, the CO generation rate of BiOBr$_{0.6}$Cl$_{0.4}$ (15.86 μmol g$^{-1}$ h$^{-1}$) was roughly 7.5 and 10.2 times as high as that of single BiOBr (1.55 μmol g$^{-1}$ h$^{-1}$) and BiOCl (2.11 μmol g$^{-1}$ h$^{-1}$), respectively. In addition, the solid solution can also be fabricated by cationic substitution in the whole composition range. Cadmium and zinc sulfide solid solution (Cd$_{1-x}$Zn$_x$S $x = 0.2, 0.4, 0.6, 0.8, 1$) were successfully constructed for CO$_2$ reduction under visible light ($λ = 450$ nm) in gas phase.\cite{291} With the increase in cadmium concentration, the light harvesting of Cd$_{1-x}$Zn$_x$S samples are orderly extended to visible-light region (Figure 14b,c). The prepared Cd$_{1-x}$Zn$_x$S solid solution produced CO as the major product in CO$_2$ reduction process (Figure 14d,e), with optimal ratio of Cd$_{0.25}$Zn$_{0.75}$S showing the highest activity of CO evolution with a rate of 2.9 μmol g$^{-1}$ h$^{-1}$ and a high selectivity of 95%.

The replacement of components in similar element composition was also carried out to form solid solution. Yan et al.\cite{292} synthesized ZnGa$_2$O$_4$/Zn$_2$GeO$_4$ solid solution. Construction of this solid solution resulted in not only narrowed bandgap, upshifted VB position (0 2p-Zn 3d) and downshifted CB position (Figure 14f,g), but also reduced hole effective mass, which was beneficial to promoting holes transfer. So, the ZnGa$_2$O$_4$/Zn$_2$GeO$_4$ solid solution exhibited improved water oxidation and protons mobility for CO$_2$ photoreduction. As a result, the optimal mole ratio of ZnGa$_2$O$_4$ to Zn$_2$GeO$_4$ is 4:5:1 and the CH$_4$ yield of this optimal sample (0.5 μmol in the first hour) is about 33 times as high as that of ZnGa$_2$O$_4$ (0.015 μmol h$^{-1}$). Liang and Li\cite{293} synthesized the Zn$_{1.231}$Ge$_{0.689}$N$_{1.218}$O$_{0.782}$ solid solution wrapped by ultrathin N-doped graphene. As an electron reservoir, N-graphene accepted electrons from ZnGeON solid solution and thus benefited the separation of electron–hole pairs for enhancing the CH$_4$ formation.

Other abundant ternary systems, such as InGaN\cite{294,295} and CdSe\cite{296,297} and some quaternary systems including ZnCdSe\cite{298} or GaN–ZnO\cite{299} are also potential photocatalysts in CO$_2$ reduction. Notably, solid solution semiconductors with delicate microstructures, including QDs, NWs, nanosheets, have more advantages than the corresponding bulk materials. In some solid solution systems, defects can be generated due to the different lattice constant, and more defects will directly impair the optical or electrical properties of semiconductors. Especially for the volatile elements, such like Zn, As, a large amount of vacancies are easy to be formed in their solid solutions. Thus, it is necessary to control the synthetic parameters, such as the reaction temperature and annealing process, to tune the concentration of vacancies.

Solid solution as homogenous phase has a uniform structure and composition distribution. According to Hume-Rothery rules, only if solute and solvent atoms have similar radius and valence of iron, these substitutinal solid solutions would be successfully synthesized rather than divided into several phases. But heteroatom doping usually has a boarded span of element choices and only focuses on specific areas. These extra dopants mainly affect the band structure and tune the electronic and surface properties of materials. Recently, it has been reported that the sublattice doping enables the fuzzy boundary of solid solution and heteroatom doping,\cite{300,301} which may provide a novel avenue to tune crystalline and band structures of 2D materials, such as graphene, MoS$_2$.

### 5. Surface Structure Engineering

After the photogenerated charges migrate from the bulk to the reactive sites on the surface, they are consumed by the adsorbed reactants for completing the potential redox reactions. Surface structure engineering with suitable strategies can boost the CO$_2$ or H$_2$O adsorption on the photocatalysts and finally activate these molecules to efficiently react with electrons or holes on the surface for CO$_2$ reduction.\cite{302,303} In other words, the performance and final products of CO$_2$ photoreduction are greatly determined by the surface structure that involves surface compositions, acidity, specific surface areas, pores, etc. The strategies for surface structure engineering of semiconductor photocatalysts can be divided into crystal facets manipulation and surface structure modification.

#### 5.1. Crystal Facets Manipulation

##### 5.1.1. Exposed Reactive Facet

In general, facets have an influence on the photocatalysis in two aspects. First, surface atomic arrangements of specific facet have effect on the molecular adsorption and intermediate products.\cite{305–308} Namely, the conversion and final products of CO$_2$ reduction can be tuned by exposed facets. Second, the band bending may occur on the surface, and diverse exposed facets are link to the redox abilities of charge carriers in reactions.\cite{309–311} In addition, the charge separation efficiency is also related to crystal orientations, as different facets has diverse atomic composition with varied charge densities.

The integration of exposed facets and noble metal loading are demonstrated as a practicable strategy to enhance photoreduction of CO$_2$. For example, the tunable performance of CO$_2$ to CH$_4$ on anatase TiO$_2${001} facets (TiO$_2${001}) and TiO$_2${010} facets (TiO$_2${010}) was achieved by loading platinum. Without Pt loading, the pristine TiO$_2${010} had a higher performance than pristine TiO$_2${001}, because TiO$_2${010} was in more favorable of CO$_2$ adsorption and prolonging the lifetime of electrons and holes. After loading 1 wt% Pt, the charge lifetime of TiO$_2${001} showed an obvious increase from 0.65 to 0.84 ns, but that of TiO$_2${010} loaded with 1 wt% Pt only increased by 0.02 ns. The CH$_4$ production rate of TiO$_2${001} with 1 wt% Pt was as twice as that of TiO$_2${010} with 1 wt% Pt. Therefore, it was proposed to produce a synergy effect between Pt-loading and certain exposing facets of TiO$_2$ for extending charge lifetime and promoting CH$_4$ production.

Similarly, the noble metal loading on specific exposing facets of BiVO$_4$ was also reported to extend the lifetime and transfer route of charge carriers. The Au photodeposition over BiVO$_4$...
Figure 14. SEM image of a) from left to right: BiOCl, BiOBr0.6Cl0.4, and BiOBr. Adapted with permission.\(^{[290]}\) Copyright 2019, Elsevier. b) UV–vis diffuse reflectance spectra and c) Tauc plots for the synthesized photocatalysts. d) CO and e) CH₄ formation over the samples Cd₀.₀–Cd₁.₀. Adapted with permission.\(^{[291]}\) Copyright 2019, The Royal Society of Chemistry. Energy band structures of zinc gallogermanate solid solution, ZnGa₂O₄, and pseudo-cubic cubic Zn₂GeO₄. f) Constructed model of zinc gallogermanate solid solution by connecting both (001) surfaces of ZnGa₂O₄ and Zn₂GeO₄. g) PDOS of ZnGa₂O₄ on the top, PDOS of Zn₂GeO₄ on the middle, and PDOS of zinc gallogermanate solid solution on the bottom. Adapted with permission.\(^{[292]}\) Copyright 2013, Wiley-VCH.
exposed by [010] and [110] facets demonstrated that the [010] facets were covered by Au particles with a size of 30–60 nm, but no Au particles were observed on BiVO₄-[110] facets (Figure 15a–c). The lifetime of photogenerated charges in BiVO₄-[010]–Au (r2) increased to 0.87 ns from 0.43 ns in pristine BiVO₄, but that of BiVO₄-[110]–Au only increased to 0.74 ns. It manifested that the electrons were accumulated on [010] facet, and the Au deposition prolonged the carrier lifetime (Figure 15i–q). By growing CuₓO on the Au surface (Figure 15d–h), the charge carriers lifetime (r2) of BiVO₄-[010]-Au–CuₓO was further increased to 1.0 ns, while that of BiVO₄-[110]–Au–CuₓO only rose to 0.79 ns from 0.74 ns (Figure 15m–q). It can be ascribed to that the photogenerated electrons from BiVO₄ were depleted by holes from CuₓO, resulting in a longer electron lifetime on the CuₓO surface.

5.1.2. Facets Junction

Different facets with diverse atomic compositions show distinct functions for accumulating the photogenerated electrons or holes. Herein, exposure of multiple facets in semiconductors to construct a facet junction can propel the electrons or holes to migrate to respective facets, achieving efficient spatial charge separation on the surface. Meanwhile, it is also desirable that the separated electrons and holes can separately participate in the reduction and oxidation, helpful to the high photocatalytic CO₂ reduction.

Anatase TiO₂ single crystal is an ideal model for exposing multiple facets. It was reported that the [100] and [010] facets have high reducing ability, and the strong oxidizing ability was observed for [001] facet in TiO₂ single crystal. Facets junction in coexposed [001] and [010] facets were developed by Cao et al. in anatase TiO₂ nanocrystals (10–30 nm); the ratio of [001] facets can be adjusted from 5% to 51%. Due to the coexposed facets promoting charge separating, the highest performance for CH₄ production from CO₂ observed in anatase TiO₂ nanocrystals (TiO₂-0.2HF) with 51% [001] and 49% [101] facets, with a CH₄ evolution rate of 1.58 mol h⁻¹ g⁻¹. A facets junction built by [001] and [010] facets was developed by Yu et al. It was theoretically predicted the electrons were more prone to move to [010] facets, and holes migrated to [001] facets under light irradiation. Meanwhile, the yield of the final products was greatly affected by the facets ratio in this facet junction, and the best ratio of [010]/[001]facets was determined to be 45:55 for CH₄ evolution. Similar facet-selective charge separation behaviors were also discovered for BiVO₄ single crystals. Li et al. fabricated the [010]/[110] facets junction over monocrystalline BiVO₄ crystal for efficient charge separation. Under solar illumination, the reduction reaction occurred on [010] facets, whereas the oxidation reaction took place on [110] facets. For confirmation, the photodeposition of metals and metal oxides were conducted. As shown in Figure 16a–f, the [010] facets were covered by metals (e.g., Au, Pt, and Ag), whereas the [110] facets were dispersed only by metal oxides (MnO₂ and PbO₂), which verified the facet-selective charge separation behaviors of BiVO₄ and the positive role of [010]/[110] facets junction in charge separation.

For a thin-layered facets junction photocatalyst, the thickness and ratio of exposing facets should be considered simultaneously. Our group reported the preparation of thickness-tunable BiOIO₃ nanoplates with [010]/[100] facet junctions by controlling the reaction conditions. Reducing the thickness along [010] direction promoted the charge carriers diffusion from bulk to the surface, and a suitable thickness assured the rational distribution of electrons on [010] facets and holes on [100] facets, realizing the efficient spatial separation of charge carriers (Figure 16g–k). It was confirmed by the observation for facet-selective photodeposition of Pt and MnO₂. As a result, BiOIO₃ nanoplates with optimal thickness exhibited the highest CO evolution rate (5.42 μmol g⁻¹ h⁻¹), ≈3 times higher than that of pristine BiOIO₃ (1.77 μmol g⁻¹ h⁻¹). Generally, the transfer of charge from semiconductors to metals is much faster (<20 fs) than that from metals to semiconductors (>20 fs). Noble metals can be deposited on the active crystal facets to further improve the charge separation efficiency and enhance CO₂ photoreduction activity. Li et al. developed brookite TiO₂ nanocubes with dominantly exposed four (210) and two (001) facets. The amount of Ag loading and the distribution of Ag NP exerted a significant influence on the performance of CO₂ photoreduction. The 0.5% Ag-TiO₂ showed the highest CO production rate (128.8 ppm h⁻¹), ≈5.41 times as high as that of the pristine TiO₂ (23.8 ppm h⁻¹). The 1% Ag–TiO₂ had the largest yield of CH₄ (28.8 ppm h⁻¹), about 3.80 times more than that of the pristine TiO₂ (7.56 μmol g⁻¹ h⁻¹). With a low Ag mass loading level (<0.5%), the majority of Ag NPs were dispersed on the (210) facets, which was conducive to producing CO from CO₂ reduction. With a larger Ag-loading amount (>0.5%), Ag NPs tended to aggregated on (210) facets and dispersed on (001) facets, which benefited the CH₄ generation. These results show that the Ag loading on different facets exerts great effects on the activity and final products of CO₂ reaction. In anatase TiO₂ nanocrystals, the photogenerated electrons are likely accumulated on (001) facets, which bene ed the CH₄ generation. Meanwhile, Pt–Ru NPs exhibited a high selectivity of CH₄ (29.7%) with an AQE of 93.7%.

The report of synthesis TiO₂ with different exposed facets always precedes the study of their photocatalytic properties in CO₂ reduction. Thus, some new trends in CO₂ reduction can be proposed from the development of TiO₂ with new facets. Basically, anatase–TiO₂ (001) planes showed a high surface energy of 0.90 J m⁻² and the dissociative adsorption of water molecules might be associated with the (001) surface by some theoretical predictions. In 2008, Yang et al. first reported that anatase TiO₂ single crystals exposed with two dominant (001) surfaces and eight (101) surfaces (Figure 17a). Anatase TiO₂ with [110] facets is very difficult to be synthesized because of the much higher surface energy of (110) facets (1.09 J m⁻²) than that of (001) facets. In 2010, Liu et al. first reported the preparation of anatase TiO₂ crystals with major (101) and (001) facets and minor (110) facets (Figure 17b,c). After the successful synthesis of TiO₂ crystals with diverse facets, the major task will...
Figure 15. a) XRD patterns of the as-prepared samples. SEM images of the as-synthesized b) BiVO₄ truncated octahedron, c) BiVO₄{010}–Au, d) BiVO₄{110}–Au, e) BiVO₄{010}–Au–Cu₂O, and f) BiVO₄{110}–Au–Cu₂O. g) TEM and h) elemental mapping images of the Au–Cu₂O core–shell heterostructure, and the corresponding HRTEM image is shown in the inset of (g). i) Steady-state PL spectra of the as-prepared samples determined for individual BiVO₄ crystals under 488 nm laser irradiation. Single-particle fluorescence imaging on j) BiVO₄ single-crystal particles, k) BiVO₄{010}–Au, l) BiVO₄{110}–Au, m) Cu₂O, n) BiVO₄{110}–Au–Cu₂O, o) BiVO₄{110}–Au–Cu₂O, and p) BiVO₄{010}–Cu₂O. Scale bars are 1 μm. q) PL decay traces of the as-prepared samples and their corresponding fluorescence lifetimes are shown in the inset of (q) (BiVO₄, Au and Cu₂O are denoted as B, A, and C, respectively). Adapted with permission.© 2018, Wiley-VCH.
be tuning the ratio of different facets and combining of two or more facets to form facet junctions.

Single crystals with specific facets have advantages of reactants adsorption and long-range electronic connectivity for CO₂ reduction. In addition, mesoporous structure is equally important in CO₂ photoreduction for enhancing light absorption and increasing potential active sites. The integration of constructing single crystalline and mesoporous in TiO₂ crystals may be a solution to fulfill both demands. Crossland et al. developed specific faceted and mesoporous single crystals of anatase TiO₂ (Figure 17d–g). It was revealed that the specific surface area of the samples was 70 m² g⁻¹, which was very similar to those of 20 nm NPs. The integration of single crystal and mesoporous structure for photocatalytic CO₂ reduction are pending research.
5.2. Surface Structure Modification

5.2.1. Surface Acid–Base Sites and Vacancy

Acidic sites on the surface of photocatalysts are beneficial for CO2 reduction as well as for specific molecular bonding, which depends on their adequate separation of photogenerated charge carriers. Proper surface acid sites grown on the Nb2O5 photocatalyst can control the activity and selectivity of CO2 conversion. It was proved that CO and HCOOH were produced under high surface acidity, while low surface acidity tended to generate CH4. In addition, the H2SO4-modified TiO2 nanosheets showed the highest CH4 yield of 13.20 μmol g⁻¹ in 4 h, and the TON and quantum yield of CH4 evolution were 83.124 and 0.726‰, respectively. The prominent catalytic activity was attributed to that the surface protonation derived from acidification with H2SO4 extended the lifetime of photogenerated electrons and holes.

Due to the acidic character of CO2, basic sites are more likely for adsorption and further to react with CO2 by electron transfer. When acid and base sites are both built on the surface, they can cooperatively promote the CO2 reduction. Dong et al. demonstrated that the Lewis acidity and basicity sites were simultaneously constructed on the surface of In2O3–x(OH)y with extra In³⁺ with Bi³⁺. The bismuth ion hybridized with oxygen causing an increased Lewis basicity. Bismuth ion also is an acid site to promote hydrogen splitting for efficient CO2 reduction. All the samples showed decent stability in 12 h (Figure 18a), and Bi-0.03% exhibited the highest activity for CO evolution with a rate of 1.32 μmol g⁻¹ h⁻¹ (Figure 18b).

A strong interaction between OVs and H2O molecules have been revealed by scanning tunnel electron microscope (STEM). Meanwhile, CO2 molecules adsorbed at surface OVs were in favor of the CO2 reduction into CO. Di et al. reported Bi12O17Cl2 superfine nanotubes with surface oxygen defects, leading to accelerated charge carriers migration and facile CO2 activation. In liquid system without cocatalyst and sacrificing reagents, Bi12O17Cl2 nanotubes delivered high selectivity toward CO with an evolution rate of 48.6 mmol g⁻¹ h⁻¹ (16.8 times than of bulk Bi12O17Cl2), and meanwhile maintained high stability after 12 h of testing. In addition, OV defects on the surface lowered the energy barrier of the CO2 reduction reaction by activating CO2 or H2O, and the simultaneous activation of H2O and CO2 molecules for matching two half reactions may be achieved by introducing OV defects on...
nanotubes. Lu et al.\cite{330} developed LaTiO2N modiﬁed by OVs and La2O3. Electron paramagnetic resonance (EPR) signal at \(g = 2.003\) was found in all the as-prepared samples, assigning to unpaired electrons trapped by OVs (Figure 18c). Two peaks located at 457.4 and 456.3 eV in X-ray photoelectron spectroscopy (XPS) (Figure 18d), in good agreement with Ti4+ and Ti3+ species, respectively. Meanwhile, the peak at 531.2 eV belonged to lattice oxygen atoms in the vicinity of OVs (Figure 18e). Due to O2− in La2O3 as basic sites, the adsorbed CO2 tended to be transformed into CO32− species, which was greatly conductive to bending O=C−O bond and decreasing LUMO energy of CO2 molecules. The OVs of LaTiO2N were beneﬁcial in activating H2O molecules, which promoted the reaction of water oxidation (Figure 18f,i). As the CO2 and H2O were activated at separate active sites (Figure 18f,i), the CH4 yield was increased to 0.3 \(\mu\)mol g\(^{-1}\) h\(^{-1}\) (Figure 18g,h).

5.2.2. Surface Modiﬁcation

The surface modiﬁcation on semiconductor photocatalysts by complexes or ions can not only extended their light absorption range to visible region or even the infrared (IR) regions, but also promoted the surface charge separation. Consequently, the ﬁnal products in reactions may vary greatly by surface modiﬁcation.\cite{331–333}

Wang et al.\cite{272} reported that the modiﬁcation of hydroxylated commercial TiO2 (P25m) with Cu(II) tetra(4-carboxylphenyl)porphyrin (CuTCP) as sensitizer, which allowed a broader spectrum of light absorption and higher separation efﬁciency than pristine P25m. In this case, 0.5%CuTCP/P25m generated almost 46 times as high CH4 as P25m alone under UV–vis irra-diation. Wang et al.\cite{272} reported that porous hypercrosslinked polymer-TiO2-functionalized graphene (HCPs-TiO2-FG) composite structure was prepared. The integration of HCPs and FG endow TiO2 with large improvement on photoabsorption, charge separation efﬁciency and CO2 adsorption as well as CO2 diffusion (Figure 19a). Speciﬁcally, the visible-light absorption and charge separation efﬁciency of TiO2 photocatalyst were improved by the graphene and the HCPs layers. HCPs layers also improved the speciﬁc surface area and increased micropore volume to 988 m\(^2\) g\(^{-1}\) and 0.306 cm\(^3\) g\(^{-1}\), respectively. As a result, this composite showed high photocatalytic CO2 reduction performance, casting a CH4 production rate of 27.62 \(\mu\)mol g\(^{-1}\) h\(^{-1}\) and selectivity of 83.7%, without sacrificial reagents and cocatalysts.

Figure 18. a) CO production rate from photocatalytic CO2 reduction on Bi-0% to Bi-0.5% samples. b) Plot of average CO production rate (black) and surface-normalized CO production rate (red) as a function of the Bi doping level during synthesis. Adapted under the terms of the Creative Commons CC-BY license. Copyright 2018, The Authors, published by Wiley-VCH. c) EPR, d) Ti 2p, and e) O 1s core-level XPS spectra for xLa2O3/LaTiO2N (x = 0.5 and 0.3) and pure-LaTiO2N. And for xLa2O3/LaTiO2N (x = 0.5 and 0.3) and pure-LaTiO2N: f) FT-IR spectra for the photocatalysts after CO2 adsorption for 2 h under the dark. g) CH4 generation over LaTiO2N with different mole amounts of La2O3 as a function of irradiation time. h) The average CH4 production rate over LaTiO2N with different mole amounts of La2O3 under another 7 h irradiation except the ﬁrst hour. i) The energies of CO2 and H2O over La2O3 (002) and LaTiO2N (002) with OVs. The calculated energies of La2O3 (002) and LaTiO2N (002) with OVs were 12 174.0 and 6792.6 eV, respectively. Adapted with permission.\cite{330} Copyright 2017, Wiley-VCH.
Metal complexes have been widely used to achieve the surface modification on different photocatalysts. Mesoporous C₃N₄ coupled with a Ru(II) binuclear complex (RuRu₂⁺) was able to selectively reduce CO₂ into HCOOH under visible light (λ > 400 nm). Integrating C₃N₄ with RuRu₂⁺ produced a new absorption band located at 460 nm, and an increase in loading amount of metallic Ag was accompanied by a new absorption band at 500–800 nm. Thus, RuRu₂⁺/Ag/C₃N₄ photocatalyst exhibited an extremely high TON (>33 000 with respect to the amount of RuRu₂⁺), while maintaining high selectivity (87–99%) for HCOOH production (Figure 19b–e). Kuriki et al.[336] explored the surface modification of CNSs rather than bulk C₃N₄ with RuRu₂⁺ and with Ag NPs for CO₂ photoreduction to produce HCOOH in aqueous media. It also showed high selectivity (≈98%) and high TON beyond 2000. With the same Ru(II) binuclear complex, a layered perovskite oxynitride of Li₂LaTa₂O₆N with RuRu₂⁺ was synthesized for visible-light CO₂ reduction.[337] RuRu₂⁺ modified Li₂LaTa₂O₆N had a visible-light absorption (wavelength > 400 nm). The selectivity and TON for CO₂ reduction into HCOOH were over 97% and 50, respectively.

Figure 19. a) Construction of a well-defined porous HCP-TiO₂-FG composite structure. (I) The functionalization of TiO₂-G by diazonium salt formation. (II) The knitting of TiO₂-FG with syn-PhPh₃ by solvent knitting method. The magnified model in top right corner is the cross profile of HCP–TiO₂–FG composite. Adapted with permission.[272] Copyright 2019, Nature Research. (b) Photocatalytic performance of CO₂ reduction that generated HCOOH over RuRu₂⁺/Ag (5.0 wt%)/C₃N₄ as a function of the loading amount of RuRu₂⁺. c) Time course of CO₂ reduction over RuRu₂⁺ (0.5 μmol g⁻¹)/Ag (5.0 wt%)/C₃N₄. Reaction conditions: 4.0 mg of photocatalyst, 4.0 mL of 4:1 (v/v) DMA/TEOA. d) Time course of CO₂ reduction over RuRu₂⁺ (3.4 μmol g⁻¹)/Ag (1.5 wt%)/C₃N₄. Reaction conditions: 4.0 mg of photocatalyst, 4.0 mL of aqueous EDTA·2Na solution (10 mM). e) Z-Scheme CO₂ reduction using a hybrid of C₃N₄ and a binuclear Ru(II) complex. Adapted with permission.[335] Copyright 2016, American Chemical Society.
To explore the photoinduced charge transfer mechanism in surface organics (electronic donor)–catalyst–acceptor system, a mononuclear C₅H₅–RuH complex oxo-bridged TiO₂ hybrid was developed by Huang et al.[338] (Figure 20a,b). C₅H₅–RuH served as the photon harvester and water-oxidation sites, whereas TiO₂ played the role of electron collector and CO₂ reduction sites. The fast electron injection from the excited Ru²⁺ cation to TiO₂ (≈0.5 ps) and the slow backward charge recombination in half life (≈9.8 μs) resulted in a substantially boosted charge separation along the donor–catalyst–acceptor pathway (Figure 20c,d), thus giving rise to a quantum efficiency of 0.56% for CH₄ production under visible-light irradiation. To pursue a nonprecious metal system with low cost, CdS QDs as photocatalysts modified with nickel terpyridine complexes were developed by Kuehnel et al.[91] The anchoring of [Ni(terpy)₂]²⁺ complexes allowed CdS QDs a high average external quantum efficiency of CO production (with over 90% selectivity) of 0.28 ± 0.04% in aqueous solution under 400 nm light (1.5 mW cm⁻²). In addition, surface decoration with inorganic ions also shows large potential. Our group reported that surface halogenation is a desirable strategy to increase the CO₂ reduction activity of Bi₂O₂(OH)(NO₃) (BON). The halide ions (Cl⁻, Br⁻, I⁻) were found to bonded with Bi atoms by replacing surface hydroxyls, which consumedly promoted the local charge separation. Furthermore, the surface grafted halide ions activated the surrounding hydroxyls to boost the adsorption of CO₂ molecules and protons for facilitating the CO₂ conversion.[178] Without any sacrificial agents or cocatalysts, Br⁻-modified BON showed the highest CO production rate (8.12 μmol g⁻¹ h⁻¹) among BON-X (X = Cl, Br, and I) samples, which was ≈73 times as high as pristine BON (Figure 20e,f).

Different surface modification methods, including regulation of acid and basic sites, introduction vacancies or grafting metal complexes and inorganic ions, were developed to tune to surface...
structure of photocatalysts, which play critical roles in enhancing light absorption and charge separation, increasing active sites, and lowering the activation energy of CO$_2$ or H$_2$O molecules, drastically optimizing the activity of CO$_2$ reduction and selectivity of products.

6. Interfacial Structure in Heterojunction

Heterojunctions includes the metal–semiconductor junctions, such as Schottky junction, and semiconductor–semiconductor junctions. In a band alignment of two semiconductors, there are five kinds of heterojunctions that can be built, as shown in Figure 21a–e. Clearly, the type I-1 as a n/n junction has superior holes separation character, and type I-2 as a p/n junction tends to realize the separation of photogenerated carriers. The type II-1 or direct Z-scheme junction is n/n junction, in which the holes with weak oxidizing capacity recombine with electrons from neighboring semiconductor, whereas holes with strong oxidizing capacity and electrons with strong reducing capacity are kept for the following surface reactions. The type II-2 or called p–n junction can also separate electron–hole pairs by hindering their recombination, but holes and electrons with weak oxidation or reduction are saved.\cite{342} The interface is an important parameter in heterojunction system. Interfaces between two adjacent components play a vital role in charge carriers transfer, because the structure of interface impacts electron–hole pair migration from light-harvesting component to surface active sites.\cite{342–345} As a typical metal–semiconductor junction and one of the most desirable semiconductor–semiconductor junctions, Schottky junction and Z-scheme junction will be discussed here.

6.1. Interface in Schottky Junction

In a combination of the metal and n-type semiconductor, the electrons present the majority of charge carriers, and their work function are $\phi_m$ and $\phi_s$, respectively. If $\phi_m > \phi_s$, the electrons in semiconductors with high Fermi level are tend to transfer to the metal with low Fermi level for achieving the equilibrium (Figure 22). The Helmholtz double layer is created at the interface of metal (negatively charged) and semiconductor (positively charged). Free charge carriers in the semiconductor usually show a low concentration. The band edges are shifted continuously originating from the presence of depletion and accumulation layers, which is called band bending, and thus it takes the energy bands upward bend. On the contrary, the band edges bend downward if $\phi_m < \phi_s$. The work function of metal minus that of semiconductor equal to the degree of band bending of semiconductor at the interface, as shown by Equation (2)

$$V_{BB} = |\phi_m - \phi_s|$$  \hspace{1cm} (2)

Only if an n-type semiconductor with $\phi_m > \phi_s$, the Schottky barrier ($\phi_{SB}$) can be established at the metal–semiconductor interface. This barrier transfer electrons from semiconductor to metal and obstruct backflow, causing a high photocatalytic performance.\cite{346–350}

Lu et al.\cite{76} established a Schottky junction in KOH-modified Ni/LaTiO$_2$N for CO$_2$ photoreduction under visible light. The yield of KOH-modified Ni/LaTiO$_2$N was $9.69 \mu$mol g$^{-1}$ for CH$_4$ and $0.31 \mu$mol g$^{-1}$ for CO, which reached 5 times as high as those of LaTiO$_2$N. In the Ni/LaTiO$_2$N Schottky junction, nickel has a large work function of 5.2 eV, which enables an upward band bending in LaTiO$_2$N close to the Ni/LaTiO$_2$N interface. The large Schottky barrier allows the formation of a built-in electric field, greatly boosting the charge separation (Figure 22). In addition, the OH$^-$ from KOH on the surface activated CO$_2$ to transform into CO$_3^{2-}$ species, and enhanced the kinetics of CO$_2$ reduction. Chen et al.\cite{351} constructed a Schottky junction in TiO$_2$/Pt on the titanium substrate (Figure 23a,b). Under equilibrium, a Schottky barrier has been established at the TiO$_2$ and Pt interface. As Pt has a higher work function than TiO$_2$, the electrons were prone to migrate from TiO$_2$ to Pt, and at the

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**Figure 21.** Schematic illustration for photogenerated charge transfer process in five types of heterojunctions with internal electric field: a) type I-1 (n/n junction), b) type I-2 (p/n junction), c) type II-1/direct Z-scheme (n/n junction), d) type II-2 (p-n junction), and e) type III-1. Reproduced with permission.\cite{339} Copyright 2019, American Chemical Society.
Figure 22. Energy band diagrams of metal and n-type semiconductor contacts. $E_{\text{vac}}$, vacuum energy; $E_c$, energy of CB minimum; $E_v$, energy of VB maximum; $\phi_m$, metal work function; $\phi_s$, semiconductor work function; $\chi_s$, electron affinity of the semiconductor. Reproduced with permission.[246] Copyright 2012, American Chemical Society.

Figure 23. TEM images the inverse TiO$_2$/Pt opals (a) and its amplification (b) obtained from 140 nm polystyrene spheres as a template. Adapted with permission.[151] Copyright 2010, American Chemical Society. TEM images of (c) Pt/MIL-125/Au. Adapted with permission.[157] Copyright 2018, Wiley-VCH. Electrostatic potentials for d) BiVO$_4${010}–Au and e) BiVO$_4${110}–Au interfaces obtained from first-principles calculations. f) Schematic diagrams illustrating the surface potential positions of BiVO$_4$ {010} and {110} and the Fermi level position of Au. Adapted with permission.[476] Copyright 2018, Wiley-VCH.
meantime holes transferred to the TiO₂ driven by this Schottky barrier. Thus, the TiO₂/Pt system showed a highly efficient separation of charge carriers. Xiao et al. evaluated the difference of electrons transfer between BiVO₄ {010}–Au and BiVO₄ {110}–Au interfaces. A Schottky junction existed at the BiVO₄ {010}–Au interface, due to the lower potential of gold (1.07 eV) than BiVO₄ {010}. Thus, a directional electron movement from BiVO₄ {010} to Au was promoted and the backflow was hindered. But an electron diffusion layer is constructed at BiVO₄ {110}–Au interface, due to the little higher potential of gold (1.07 eV) than BiVO₄ {110}. This electron diffusion layer impeded the migration of electrons from BiVO₄ {110} to Au, resulting in reduced electrons transfer at the interface (Figure 23d–f).

The encapsulation of metal NPs for Schottky junctions has been developed to improve the transfer of electrons and holes. Interestingly, it was highlighted that the integration of plasmonic effect and Schottky junctions has the potential to enhance visible-light harvesting and photoinduced charge carries separation for high photocatalytic activity. For example, copper with plasmonic effect was encapsulated in UiO-66 to form Schottky junctions (Cu/Cu@UiO-66). The photocatalytic performance of Cu/Cu@UiO-66 was enhanced by encapsulating a very low concentration of Cu, which attributed to a synergy of plasmonic effect and Schottky junctions to allow the visible-light absorption and electron capture. Also, the plasmonic Au was combined with Pt-MOF Schottky junction to develop a Pt@MOF/Au system. In this ternary photocatalyst, Pt NPs were well dispersed into or on MIL-125, followed by assembly with Au nanorods. As a result, both high visible-light harvesting and efficient charge transfer were achieved in Pt@MOF/Au system, attributing to the Au plasmonic resonance and Pt-MOF Schottky barrier.

### 6.2. Interface in Z-Scheme Junction System

Z-scheme junction integrating dual photocatalysts and interface is an efficient way to mimic photosynthesis in nature, which contains two parts in plants, photosystem (PS) I and II. Electrons are produced in PS I and consumed in the CO₂ reduction, whereas the holes are produced in PS II and tend to generate O₂ from H₂O oxidation (Figure 24a,b). The fabrication of Z-scheme can prolong the charge carriers lifespan and meanwhile maintain the strong redox capabilities. For example, Li₂LaTa₂O₆N has an advantage of proper band structure for water oxidation and CO₂ reduction, but it suffers from low product selectivity.

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### Figure 24

Comparison of a) biological photosynthesis and b) dual n-type semiconductor model, representing the electron transport chain and redox potentials. Adapted with permission. Copyright 1979, Elsevier. Schematic charge-transfer mechanism in three kinds of Z-scheme photocatalytic systems: c) liquid-phase, d) all-solid-state, and e) direct Z-scheme. Adapted with permission. Copyright 2019, American Chemical Society.
from the various CO₂ reduction pathways. The Ru(II) binuclear complexes with excellent visible-light absorption have a strong ability to reduce CO₂ to HCOOH with a high TON. Due to the low oxidation capability of Ru(II) binuclear complexes, an electron donor is necessary for keeping reasonable stability and conversion rate during the CO₂ photoreduction. Thus, Ru(II) binuclear complexes as reduction part couples an oxidation catalyst Li₂LaTa₂O₆N to build a delicate Z-scheme system, which solved the aforementioned problems for a high yield of HCOOH with a high stability. So far, there are mainly three types of Z-scheme systems reported in photocatalysis, namely, liquid-phase Z-scheme junction, all-solid-state Z-scheme junction with a mediator, and direct Z-scheme junction (Figure 24c–e).[35]

6.2.1. Liquid-Phase Z-Scheme Junction

In 1979, liquid-phase Z-scheme photocatalytic system in semiconductors was first proposed by mimicking photosynthesis in plants (Figure 24a). The semiconductor–solution interface controls the charge transfer processes, which can reduce the recombination photogenerated charges to improve the stability and activity of photocatalysts. In 2001, a liquid-phase Z-scheme photocatalytic system was established with Pt@anatase-TiO₂ and primary rutile-TiO₂ in the existence of IO₃⁻/I⁻ as the shuttle redox mediator for overall water splitting.[166] In addition, liquid-phase Z-scheme system of BiOI/g-C₃N₄ was constructed to promote charge transfer by the intermediate I₃⁻ ions for the application of CO₂ photoreduction.[167] The I⁻ ions are oxidized to I³⁻ ions by the holes from BiOI and subsequently, the I³⁻ ions are reduced by electrons of g-C₃N₄, resulting in a full cycle of the I⁻/I⁻ redox mediator. Note that the liquid-phase Z-scheme systems with suitable solution usually have to tackle a potential reaction in the backward direction. For instance, the reduction of oxidative mediator (I³⁻ ions) competes with CO₂ reduction. To address this drawback, all-solid-state Z-scheme junction with an electron mediator were developed.

6.2.2. All-Solid-State Z-Scheme Junction with Mediator

In all-solid-state Z-scheme junction with mediator, the photogenerated electrons and holes move through a solid-state mediator (Figure 25a,b), which can separate and collect charge carriers from the semiconductors. Thus, the appropriate mediator with interface modification can optimize the interfacial energy of semiconductor–solid-state mediator and boost the electron transfer from semiconductor.[366–371]

Developing solid-solid interfaces in Z-scheme system provides special opportunities to create new features by combing the distinctive characteristics of different semiconductors. In 2006, Tada et al.[372] reported the preparation of CdS–Au–TiO₂ composite photocatalyst as an all-solid-state Z-scheme system (Figure 25a), in which CdS and TiO₂, respectively, served as PS I and PS II, and Au as mediator was grown at the interface between CdS and TiO₂. Thus, the photogenerated electrons from TiO₂ can cross Au to reach CdS to recombine with the holes of the latter for keeping the highly reductive electrons on the CB of CdS and highly oxidative holes on the VB of TiO₂, leading to the excellent photocatalytic activity of Au@CdS/TiO₂ (Figure 25e,f).

Similarly, RGO with super conductivity was reported to use to as an ideal mediator construct Fe₅V₅O₁₃/RGO/CdS all-solid-state Z-scheme junction for photocatalytic conversion of CO₂ into CH₄ (Figure 25b–d).[373] The RGO interlayer establishes a high-speed pathway with high electronic mobility for charge transfer between Fe₅V₅O₁₃ and CdS in Fe₅V₅O₁₃/RGO/CdS (Figure 25c), which thereby rendered a 30% increase in CO₂ reduction for CH₄ production in comparison with Fe₅V₅O₁₃/CdS (Figure 25d).

6.2.3. Direct Z-Scheme Junction

Direct Z-scheme system as a new generation of junction photocatalyst was developed, which exhibits obvious advantages than the previous Z-scheme system, such as low cost and convenient preparation.[374–379]

For example, porous g-C₃N₄/SnS₂-diethylentriamine (Pg-C₃N₄/SnS₂-DETA) composite as a direct Z-scheme system no electron mediator was constructed.[380] It displayed high production rates of CH₄ (4.84 μmol g⁻¹ h⁻¹) and CH₃OH (1.35 μmol g⁻¹ h⁻¹), which was attributed to the formation of direct Z-scheme between Pg-C₃N₄/SnS₂-DETA, promoting photogenerated charge separation. To improve the interfacial structure in Z-scheme junction, Al–O bridges were introduced in the g-C₃N₄/α-Fe₂O₃ Z-scheme system by Wang et al.[381] to reinforce the electrons transfer. The photocatalytic activities of this Z-scheme junction with Al–O bridges are higher than that without Al–O bridges in CO₂ photoreduction. This performance enhancement is resulted from the promoted charge transfer and separation provided by Al–O bridges in g-C₃N₄/α-Fe₂O₃. Further, a ternary Z-scheme photocatalyst Ag₃CrO₄/g-C₃N₄/GO was developed.[382] In this direct Z-scheme junction, improved light absorption, redox ability, and enhanced charge separation were achieved in Ag₃CrO₄/ g-C₃N₄, and meanwhile GO served as a cocatalyst further promote the charge separation and the CO₂ adsorption. Ag₃CrO₄/ g-C₃N₄/GO showed a high CH₃OH and CH₄ production with a turnover frequency (TOF) of 0.30 h⁻¹ under simulated sunlight irradiation, which was 2.3 times higher than that of pristine g-C₃N₄. It may be concluded that fabrication of ternary direct Z-scheme junction may show a larger superiority.

In contrast, the morphology control, such as 1D nanobelts,[383–387] or 2D nanosheets,[222,388–390] was introduced to enhance the photocatalytic activity of Z-scheme junction photocatalysts. To build a unique 3D morphology, Yang et al.[227] assembled 2D ZnIn₂S₄ nanosheets onto 1D TiO₂ nanobelts to form a direct Z-scheme junction ZnIn₂S₄/TiO₂. This 3D structure showed large surface area and high efficiency of charge separation where the electrons were collected in the CB of ZnIn₂S₄, whereas holes were accumulated in the VB of TiO₂, leading to an enhanced activity for CO₂ photoreduction. The evolution rate of CH₄ of 3D ZnIn₂S₄/TiO₂ (1.135 mol g⁻¹ h⁻¹) was around 39 times as high as that of bare ZnIn₂S₄ (0.029 mol g⁻¹ h⁻¹). Hexagonal WO₃ nanosheets with dominant (001) facets (WO₃-001) are more effective for H₂O oxidation, but the CB edge potential cannot meet the demand of CO₂ photoreduction. In regard to this issue, Shi et al.[391] assembled Cu₂O on WO₃-001 to construct the Cu₂O/WO₃ Z-scheme junction, which was endowed with enhanced light absorption, charge separation,
Figure 25. a) HRTEM image of Au–CdS/TiO2. b) HRTEM image recorded frame marked region in (a). Schematic illustration of photocatalytic conversion of CO2 into CH4 over Fe2V4O_{13}/RGO/CdS Z-scheme. (Fe2V4O_{13} ECB: −0.55 eV, EVB: 1.28 eV; CdS ECB: −0.52 eV, EVB: 1.88 eV vs NHE) (inset b). c) The PL decay spectra of as prepared samples. d) CH4 and O2 generation velocity of as-prepared samples. e,f) Adapted with permission.\textsuperscript{[372]} Copyright 2006, Nature Research. b–d) Adapted with permission.\textsuperscript{[373]} Copyright 2014, The Royal Society of Chemistry. e) EELS of the support (1, blue line) and shell layer (2, red line) in (a). f) Photocatalytic activity of Au@CdS/TiO2 by time courses for photocatalytic reduction of MV\textsuperscript{2−}. g) Time courses of CO evolutions. h) Average CO production rates of g-C3N4, α-Fe2O3, and α-Fe2O3/g-C3N4 hybrid, and i) Z-scheme photocatalytic system. Adapted with permission.\textsuperscript{[392]} Copyright 2018, Wiley-VCH.
and redox abilities. The CO and O₂ yields were 11.7 and 5.7 μmol under visible light (i > 400 nm) in 24 h, respectively. Jiang et al. designed an urchin-like α-Fe₂O₃/g-C₃N₄ Z-scheme junction, which was confirmed by the active radical tests.⁴¹⁹ In the absence of any cocatalysts and sacrifice agents, it demonstrated a much higher production rate of CO (27.2 μmol g⁻¹ h⁻¹), which was over 2.2 times higher than single g-C₃N₄ (10.3 μmol g⁻¹ h⁻¹), (Figure 25g,h). There are two main reasons responsible for the enhanced photocatalytic activity: on one hand, the urchin-like structure was very beneficial to the harvesting light, which contributed to the generation of more photoinduced charge carriers. Consequently, the Z-scheme structure of α-Fe₂O₃/g-C₃N₄ allowed improved charge separation and reductive ability for CO₂ reduction (Figure 25i). More examples of Z-scheme junction for CO₂ reduction are shown in Table 3.

The aforementioned junctions mainly include two types of interface structure, namely metal–semiconductor and semiconductor–semiconductor interfaces. At a metal–semiconductor interface, the charge transfer between metal and semiconductor and band bending is closely related to Schottky barrier. Z-scheme junction as a typical semiconductor–semiconductor junction for interface engineering involves solid–liquid and solid–solid interfaces, and the direction Z-scheme junction displays a larger potential for CO₂ photoreduction due to its many merits. The promotion of electrons from oxidative parts to the reductive parts is important for a doable Z-scheme junction. As a practicable strategy, it has been successfully utilized in photocatalytic CO₂ reduction and other reactions, including H₂ or O₂ evolution for overall water splitting systems.

### 7. New Trends and Strategies

#### 7.1. Exploration of New Photocatalytic Structure Systems

##### 7.1.1. MOFs and COFs

An ideal support can realize the integration of activity, selectivity, and efficiency. MOFs and COFs are emerging candidates to fulfill these challenges. The large specific surface areas and the porous network adsorption ensure the good adsorption of CO₂⁴⁹–⁵⁰ and easy tailoring on the molecular structures of MOFs and COFs with different building units allowed adjustable bandgap, optimized charge carrier transfer ability, and tunable selectivity of reductive products (Figure 26a).²⁸,⁴⁰²–⁴⁰⁵

In 2011, the first MOF for CO₂ photoreduction was developed by incorporating Re complexes into UiO-67.⁴⁰⁶ The advantage for this system was to replace original ligands para-biphenyldicarboxylic acid (bpdc) in UiO-67 by a molecular catalyst Re⁺(bpdy)(CO)₃Cl (bpdy = 2,2’-bipyridine), due to the matchable lengths between bpdc and Re complexes ligands (L₄) in UiO-67 frameworks. Using L₄ as an active linker in UiO-67 framework, the Re catalytic centers were stable in the atmosphere (at most 400 °C), and the porous MOF platform was capable of converting CO₂ to CO in an acetonitrile solution with triethyleneamine as sacrificial agent under illumination. The TON of functionalized UiO-67 was 10.9 in 20 h, which was almost 3 times as high as that of the molecular catalyst Re⁺(dcbpy)(CO)₃Cl (Figure 26b,c). Unfortunately, it was observed that functionalized UiO-67 lost catalytic activity after limited reactions.

Secondary building units (SBUs) in MOFs play a vital role in redox reactions due to their potential coordination sites. In terms of MIL-101(Fe), up to three potential open metal sites were available with the Fe-SBUs, leading to desirable adsorption and efficient CO₂ reduction. The efficient charge carrier mobility was also observed from O²⁻ to Fe²⁺ and Fe³⁺ was substantially produced in MIL-101 under visible light. Thus, a TON of CO₂ to HCOOH of 1.2 was observed for MIL-101(Fe) under 24 h visible-light irradiation using TEOA as the sacrificial agent. Furthermore, it was demonstrated that there is a strong relationship between HCOO⁻ production and the wavelength of illumination in MIL-101(Fe) system (Figure 26d–e).⁴⁰⁷ Yan et al.⁴⁰⁸ demonstrated that the combination of binuclear Eu(III)₂ SBUs and Ru(phen)₃-derived ligands to build a novel MOF, which realized the conversion of CO₂ to HCOOH under visible-light irradiation, and the HCOOH evolution reached 321.9 μmol h⁻¹ mmol MOF⁻¹ upon visible light illumination (from 420 to 800 nm). The Eu₂[μ₂-H₂O-EuI]SBUs have open metal sites and metal clusters are covered by terminal water ligands, which are favorable for the adsorption and reduction of CO₂. Under irradiation, the electrons tended to transfer from metallic ligands to SBUs to participate in the CO₂ reduction reaction and visible light can motivate binuclear [EuI₂-H₂O-EuII]active sites to finish the conversion CO₂ to HCOOH via a two-electron reduction process.

The adjustment of electronic characteristics of the SBU in MOFs is also a practicable way for promoting the photocatalysis. Lee et al.⁴⁰⁹ demonstrated Ti⁴⁺-modified Zr₆O₄(OH)₄ SBU in UiO-66 for photoreduction of CO₂ to HCOOH with matched redox potential energies between the organic linkers and SBU. The doping of Ti⁴⁺ ions in SBU enabled a lowered electron accepting levels of Zr₆Ti₄(OH)₄(OH)₄ SBUs, thus allowing a photocatalytic activity. Eventually, this Ti⁴⁺-modified UiO-66 was demonstrated to expand the light responsive range, boost the transfer of photogenerated carriers, and reduce the recombination of electrons and holes. Thus, formic acid was selectively produced from CO₂ under visible light in an acetonitrile with TEOA as the sacrificial base and 1-benzyl-1,4-dihydropyrimidine as the sacrificial reductant. This MOF achieved a TON of 6 for CO₂ reduction within 6 h, which indicated that each Ti⁴⁺ site transferred about 13 electrons to reactants over each catalytic run. Overall, MOFs as efficient supports have many benefits, such as 1) single crystals of MOFs are usually transparent, which are able to use solar light without obvious scattering and adsorption; 2) MOFs have large specific surface area with abundant reactive sites; and 3) the highly porous network of MOFs provides an easy access of the CO₂ to potential catalytically active sites (Figure 26a).

Different from MOF systems, layer-structured COFs always show efficient mobility of charge carriers.¹⁶¹ COF-366 comprising cobalt porphyrins (COF-366-Co) was reported as an electrocatalyst for CO₂ reduction. With an overpotential of −0.55 V, COF-366-Co achieved the reduction of CO₂ into CO with a yield of 36 mL mg⁻¹ over 24 h with a Faradaic efficiency of 90% in water (Figure 26f,g). With an overpotential of −0.55 V at pH 7, TON was up to 290 000, over 24 h without any obvious activity decay (Figure 26h). Covalently linked cobalt porphyrins as active sites were able to efficiently facilitate the reaction route of CO₂
Table 3. Z-Scheme photocatalysts for CO₂ photoreduction.

| Photocatalyst | Type of Z-Scheme junction | Production | Yield | Reaction condition | Ref |
|---------------|----------------------------|------------|-------|--------------------|-----|
| Ag₂CrO₄/g-C₃N₄/graphene oxide | Direct Z-Scheme | CH₄ | TOF 0.30 h⁻¹ (Total) | Full spectrum simulated sunlight | [382] |
| g-C₃N₄/Sn₂S₃-diethylenetriamine | Direct Z-Scheme | CH₄ | 4.84 μmol g⁻¹ h⁻¹ | Visible light (λ > 420 nm) | [380] |
| α-Fe₂O₃/Cu₂O | Direct Z-Scheme | CO | 1.67 μmol g⁻¹ h⁻¹ | Visible light (λ > 400 nm) | [484] |
| BiOI/g-C₃N₄ | Liquid-phase Z-Scheme | CO | 3.45 μmol g⁻¹ h⁻¹ | Visible light (λ > 420 nm) | [365] |
| Au@g-C₃N₄/SnS yolk-shell | All-solid-state Z-Scheme | CH₄ | 0.95 μmol g⁻¹ h⁻¹ | Visible light (λ > 420 nm) | [485] |
| Oxygen-defective ZnO (O-ZnO)/reduced graphene oxide (rGO)/UiO-66-NH₂ | All-solid-state Z-Scheme | CH₃OH, HCOOH | 34.83 μmol g⁻¹ h⁻¹ | Visible light (λ > 420 nm) | [486] |
| g-C₃N₄/FeWO₄ | Direct Z-Scheme | CO | 6 μmol g⁻¹ h⁻¹ | Visible light (λ > 420 nm) | [487] |
| BiVO₄/carbon-coated Cu₂O NW arrays | All-solid-state Z-Scheme | CO | 3.01 μmol g⁻¹ h⁻¹ | Visible light (λ > 420 nm) | [258] |
| rGO/InVO₄/Fe₂O₃ | Direct Z-Scheme | CH₃OH | 0.7 μmol g⁻¹ h⁻¹ | Visible light (λ > 400 nm) | [97] |
| Ag₃PO₄/g-C₃N₄ | All-solid-state Z-Scheme | CO, CH₃OH, CH₄, and CH₃CH₂OH | 57.5 μmol g⁻¹ h⁻¹ (Total) | Visible light (λ > 420 nm) | [488] |
| 3D ZnIn₂S₄/TiO₂ | Direct Z-Scheme | CH₄ | 1.135 μmol g⁻¹ h⁻¹ | 300 W Xe lamp | [227] |
| Bi₅W₈O₃r-GO/g-C₃N₄ | All-solid-state Z-Scheme | CO | 15.96 μmol g⁻¹ h⁻¹ | Visible light (λ > 420 nm) | [489] |
reduction. Moreover, COFs present high thermostability and chemical durability, due to the strong covalent bonds. Fu et al.\[410\] introduced two azine-based COFs for converting CO₂ to CH₃OH with H₂O without sacrificial agents under visible light. The activity of CO₂ photoreduction of azine-based COFs is higher than that of g-C₃N₄ semiconductors with water.

MOFs as 3D porous crystals have well-defined structure, and various metal clusters in MOFs lead to multiple advantages in light absorption, electronic structure, and catalytic active sites. Regulating organic linkers of MOFs can not only supply an extra light absorption pathway, but also increase the amount of potential active sites. The stabilities of MOFs, including water stability and photostability, are also vital factors for CO₂ photoreduction. The poor water stability limits the application of photocatalysts in aqueous solution systems. According to the hard and soft acids and bases (HSAB) theory, water stability of MOFs depends on bond strength between the ligands and metal clusters.[411] MIL-100 (Al, Fe, and Cr), MIL-125 (Ti), and ZIF-7 (Zn) have a high water stability. The photostability is another issue for MOFs, especially for hydrocarbon products evolution from CO₂ reduction. Generally, MOFs with a high connectivity number of metal clusters and ligands usually show a high photostability, such as UiO-66 and UiO-67.[412] It is worth to note that the structure collapse may occurs in MOFs during long illumination. And in this condition, MOF derivatives may realize high photocatalytic CO₂ reduction than MOFs itself.

COFs usually show high charge carrier mobility, due to the p-conjugation and p–p stacking in their reticular structure. Added nitrogen units or metal irons are usually catalytic centers in COFs, thus enabling a precise manipulation of active sites within a designed COF structure. A desirable photocatalytic MOFs or COFs system requires more photosensitive units, abundant active sites for substrates capture and reaction, as well as a decent match of bandgap between SBUs and linkers. Integrating all these functional groups in SBUs or organic linkers into MOFs or COFs will offer great potential for development of new catalytic systems in CO₂ reduction.

7.1.2. Semiconductor Biohybrids

Photosynthetic organisms develop into metabolic pathways to realize CO₂ reduction and store solar energy in chemicals.[413,414] Biologic carbon fixation has made great achievements that artificial catalysts are not able to make, such as the lifetime of enzymes and specificity of catalytic pathways.[415–421] But the light absorption capability of semiconductors is often higher than that of natural photosynthesis.[422–425] Thus, it is a promising way to solve CO₂ reduction issues by integrating high light-absorbing inorganic catalysts with photosynthetic organisms. This novel way enables to develop value-added chemicals from CO₂ reduction by solar energy. Meanwhile, the solid boundaries can be broken by developing biohybrid semiconductor photocatalysts, which is also an approach to explore their potential and complementary functions.

The pioneering work of semiconductor biohybrids photocatalysts was reported by Sakimoto et al.[426] in which CO₂ was converted into acetate by combining acetogenic bacteria with CdS NPs that have intense visible-light absorption. M. thermoacetica
was one type of acetogenic bacteria, and CdS NPs can be grown on it by simply adding Cd²⁺ and sulfur source (such as cysteine) into the cells. By enzymatic process, the sulfur was easily reduced to sulfide and then to produce CdS NPs by reacting with Cd²⁺ (Figure 27a–c). It was found that CdS was primarily growth on the membrane of mycobacterium thermoacetum. These CdS NPs produced photogenerated electrons and holes under low-intensity simulated sunlight. According to the Wood–Ljungdahl path, a reducing equivalent [H] was induced by electrons and subsequently reacted with CO₂ to produce acetic acid.
At the same time, holes reacted with cysteine to produce oxidized disulfide-bonded cystine (CySS) (Figure 27b). This photosynthetic reaction is shown in Equation (3)

$$2\text{CO}_2 + 8\text{Cys} + 8\nu \xrightarrow{\text{M. thermoacetica−CdS}} \text{CH}_3\text{COOH} + 2\text{H}_2\text{O} + 4\text{CySS}$$ (3)

Several blank experiments and tests were conducted to prove this photocatalytic mechanism, including control groups of *M. thermoacetica*, CdS, and light condition (Figure 27d). The yield of acetic acid increased with increase the intensity of blue light (435–485 nm), and a 4 times increase in quantum yield (85 ± 12%) was obtained (Figure 27e).

However, CdS NPs are dramatic poison in organisms system, which are harmful to the environments. Developing intracellular particles can further enhance photosynthetic process, which means that NPs are grown on the entire cell instead of mainly being on the membranes. Gold nanoclusters (AuNCs) show benign visible-light absorption and good biocompatibility. Zhang et al. reported that glutathione was used to combine AuNCs as intracellular NPs into a network (Figure 27f,g).

Figure 27. a) Depiction of the *M. thermoacetica*–CdS hybrid system, proceeding from the growth of the cells and bioprecipitation (loading) of the CdS NPs (shown in yellow) through photosynthetic conversion of CO₂ (center right) to acetic acid (right). b) Pathway diagram for the *M. thermoacetica*–CdS system. Two possible routes to generate reducing equivalents, [H], exist: generation outside the cell (dashed line) or generation by direct electron transport to the cell (solid line). c) high-angle annular dark field (HAADF) STEM image of a single cell, showing clusters across the entire cell surface. d) photosynthetic production of acetic acid by *M. thermoacetica*–CdS hybrids and deletion controls. e) Rates of acetic acid production and quantum yields for increasing illumination intensities and *M. thermoacetica*–CdS concentrations. Adapted with permission. Copyright 2016, American Association for the Advancement of Science. f) The Au_{22}(SG)_{18} nanoclusters were delivered into bare *M. thermoacetica* (gray) during the culture process, forming *M. thermoacetica*/AuNCs with red emission. The simulated chemical structure of Au_{22}(SG)_{18} nanoclusters is shown in the inset. Light yellow spheres, Au atoms in the core; dark yellow, Au atoms in the staple motifs; red, S atoms in the shell. All other atoms (carbon, hydrogen) have been omitted from this structure for clarity. Also shown are space-filling models of acetic acid and CO₂ (orange, oxygen; gray, carbon; white, hydrogen). g) Schematic of bacterium. The electrons generated from intracellular AuNCs under illumination are used by enzymatic mediators inside the cytoplasm and are finally passed on to the Wood–Ljungdahl pathway. h) SLM image of individual *M. thermoacetica*/AuNC photosynthetic biohybrid system (PBS). i) Normalized photosynthetic production of acetic acid by *M. thermoacetica*, *M. thermoacetica*/AuNCs, and *M. thermoacetica*–CdS PBSs under continuous low-intensity illumination and in dark conditions (n = 20 culture batches for *M. thermoacetica*–CdS (light), n = 35 culture batches for other conditions). j) PL spectra of pure AuNCs, bare *M. thermoacetica*, *M. thermoacetica*/AuNCs in CO₂-free conditions without photosynthesis ability, and *M. thermoacetica*/AuNCs in the photosynthesis process. k) Bacteria enumeration of *M. thermoacetica*/AuNCs, *M. thermoacetica*–CdS, and bare *M. thermoacetica* by colony counting in the heterotrophic medium in dark conditions. Adapted with permission. Copyright 2018, Nature Research.
Structured light microscopy (SLM) illustrated the position of AuNCs in bacteria, and also provided the distribution of AuNCs from bottom to top in hybrid systems (Figure 27h). The nonphotosynthetic bacteria can be functionalized by AuNCs penetrating to realize photosynthesis of \( \text{CO}_2 \) to acetic acid (Figure 27i). AuNCs also reduced the amount of reactive oxygen species (ROS) to keep the bacteria alive. As a result, the cell in AuNC–hybrid system demonstrated a high level of proliferation and viability rate after 12 h, but the CdS–hybrid system as a control group began to decay (Figure 27k). According to the Wood–Ljungdhal route, AuNCs produced photogenerated electrons and moved to cytoplasmic mediators in cells (Figure 27g,j). This biohybrid system was enabled to absorb photons and produce electrons to finalize metabolism in cells, which was highly dependent on the light absorption and biocompatibility of AuNCs. It was also proved that the continuous conversion of \( \text{CO}_2 \) can be efficiently achieved in several days.

With the dual advantages of AuNCs and micro-organisms, a novel pathway using solar energy was achieved to realize carbon fixation to obtain hydrocarbons. The further study of inorganic–biological interface is expected to enable the manipulation of the activity and selective of \( \text{CO}_2 \) conversion in biohybrid systems. Valuable chemical products are expected to be obtained by photosynthetic \( \text{CO}_2 \) organisms with semiconductors in the future.

7.1.3. Single-Atom Photocatalysts

Homogeneous and heterogeneous catalysis are two main branches of the catalysis family, both of which are applied in photocatalytic \( \text{CO}_2 \) conversion to produce hydrocarbons. Several advantages of homogeneous photocatalysts are depending on their atomically dispersed active sites, tunable light absorption, as well as high activity and selectivity. Heterogeneous photocatalysts with relatively low cost are easy to synthesize and facile to be extracted and recycled for long-term run. Single-site catalysts integrate the advantages from both homogeneous and heterogeneous catalysts, thus attracting great interests for photocatalytic \( \text{CO}_2 \) reactions.

Cobalt as a transition metal is efficient single-atom catalysts either on the surface or in the body of substrate materials. Incorporating Co single atoms on the partially oxidized graphene nanosheets (Co$_1$–G nanosheets) to realize \( \text{CO}_2 \) conversion was demonstrated by Gao et al. (Figure 28a). The absence of Co–Co peak in Co$_1$–G sample indicated that no Co or CoO clusters existed, and the Co species were separated into individual atoms. The Co single atoms showed many advantages, such as rich unsaturated coordination sites and variable electronic configuration that can ensure high activity and selectivity, simplified catalytic mechanism due to the straight forward metallic coordination situation. A high TON of 374 and TOF of 2.08 min$^{-1}$ for CO formation was observed in Co$_1$–G catalyst (Figure 28b), and they were further increased to 678 and 3.77 min$^{-1}$, respectively, by combining [Ru(bpy)$_3$]Cl$_2$ with Co$_1$–G nanosheets.

Combining single-atomic sites into 2D ultrathin nanosheets is a promising approach to integrate their advantages. Di et al. reported the successful synthesis of Bi$_2$O$_3$Br atomic layers with well-dispersed single cobalt atoms (Figure 28c). It was proven that the valence state of isolated and highly dispersed single Co atom is close to $+2$ (Figure 28d,e), because the position of Co K-edge absorption edge was close to that of CoO rather than Co foil in Co–Bi$_2$O$_3$Br–1. Due to Co atoms as single sites (Figure 28f,g), the activation energy barrier of \( \text{CO}_2 \) was decreased to stabilize the intermediates, such as COOH$^\cdot$. 

Figure 27. Continued.
So the bottlenecks in adsorbing intermediate COOH* and desorbing CO* were broken by constructing single Co atoms (Figure 28h). Therefore, Co–Bi3O4Br–1 demonstrated a superior CO yielding rate of 107.1 μmol g−1 Co h−1, which was about 4 and 32 times as high as that of Bi3O4Br atomic layer and Bi3O4Br bulk materials, respectively.

In summary, single atom plays a vital role for CO2 photoreduction, like lowering the activation energy barrier of CO2, and the single-atom catalysts bridge heterogeneous and homogeneous photocatalysts, showing substantial superiority in terms of highly tunable structure and robust performance.

7.2. New Structure Regulation Strategies

7.2.1. Polarity Enhancement

In noncentrosymmetric (NCS) materials, the centers of positive and negative charges do not coincide, which can produce a polarization-induced electric field to urge the migration of photocatalytic performance.

Ferroelectric structures have spontaneous dipole moment, and thus tend to generate spontaneous polarization electric field to transfer charge carriers from bulk to surface. A layered ferroelectric perovskite SrBi4Ti4O15 was prepared by our group for efficient CO2 reduction, and it was treated by annealing at 350 and 650 °C for enhancing the ferroelectricity (Figure 29a–d).262 SrBi4Ti4O15 uncovered a strong ferroelectric spontaneous polarization along [100] direction, which boosted charge separation along a axis direction in bulk (Figure 29a,d). Without cocatalysts and extra sacrificial agents, the annealed SrBi4Ti4O15 (SBTO) nanosheets at 350 °C showed a prominent photocatalytic activity.
in CO₂ reduction for CH₄ evolution in gas–solid system, with a production rate of 19.8 μmol g⁻¹ h⁻¹ and apparent quantum yield of 1.33% at 365 nm. In addition, Bi₂MoO₆ ultrathin nanosheets (BMO-U) with boosted ferroelectricity were developed for CO evolution from CO₂ photoreduction.⁴⁶³ Due to lattice distortion in ultrathin layered structure, the polarization degree of BMO-U can be further enhanced by corona poling, which causes a boosted polarized electric field along the a and c axes in BMO-U, promoting the charge separation between layers. Thus, the CO yield of polarized BMO-U (14.38 mmol g⁻¹ h⁻¹) was over 3 times larger than that of bulk Bi₂MoO₆ (4.08 mmol g⁻¹ h⁻¹), and over as 10 times as higher than that of bulk Bi₂MoO₆ (1.36 mmol g⁻¹ h⁻¹). A directional accumulation of polar units can also enhance the macroscopic spontaneous polarization, inducing the transfer of photoinduced charge carriers from bulk to surface. NCS BiOIO₃ contains aligned IO₃ polar units along the [001] direction. When BiOIO₃ grew along this specific direction (Figure 29e,f), an enhanced polarization electric field was formed from BiOIO₃ particle (BIO-S) to BiOIO₃ nanorods (BIO-L), which promoted the charge carriers transfer from the bulk to the surface (Figure 29h,i). BIO-L with abundant OVs showed a CO yield of 17.33 μmol g⁻¹ h⁻¹, which was over 10 times larger than that of BIO-S (1.68 μmol g⁻¹ h⁻¹), as shown in Figure 29g.⁴⁶⁴

Furthermore, a polarized local surface in photocatalysts facilitates charge migrates and thereby promotes redox reactions on the surface. Zhang et al.⁴⁶⁵ reported a successful synthesis of around 1 nm g-C₃N₄ layers, and further construct a polarized surface to convert CO₂ to CO with showing roughly 80% Faradaic efficiency. g-C₃N₄ characterized with ultrathin layered structure with polarized surface (2D-pg-C₃N₄) was enabled to enrich electrons. As a result, the current density of 2D-pg-C₃N₄ at −1.2 V versus Ag/AgCl is 3.05 mA cm⁻², which is almost 30 times as large as that of the bulk g-C₃N₄. An intensified electron density of ultrathin g-C₃N₄ layers was observed, because the
characteristic XPS peaks of sp² N and C atoms were shifted to lower binding energy regions. The polarized melon subunits tend to become active centers to enhance CO₂ reduction. The polarized melon subunits can act as active centers to promote CO₂ reduction over metal-free g-C₃N₄. The CO₂ desorption peak of 2D-pg-C₃N₄ was much lower than that of bulk g-C₃N₄, thus 2D-pg-C₃N₄ showed a favorable activation process of CO₂ molecules.

Therefore, it is an efficient strategy to use polarization as a useful way for reducing the recombination of electrons and holes in bulk and/or on the surface, but the research in this particular area is still in its infancy. The elemental doping is potential to enhance the polarization; precise tailoring the microstructure of photocatalysts system will also help to some content.

8. Conclusions

Structural engineering is regarded as an efficient way to solve the crucial problems that restrict the CO₂ photoreduction activity, thus resulting in the high activity, stability, and tunable selectivity of products. In this Review, the progress in this research area has been systematically summarized. First, the efficient strategies for structural design from recent works are reviewed, which are divided into five sections based on nano-/microstructure, crystalline and band structures, surface structure, and interface structure. Then, new trends and strategies for CO₂ photoreduction were introduced. Several new photocatalytic systems for CO₂ photoreduction have been introduced, including MOFs, COFs, semiconductor biohybrid systems, and single atom systems. In addition, polarization as a new strategy to enhance charge separation has been summarized. Although great achievements have been made in recent years, there is still a long way in developing structural engineering for CO₂ photoreduction. For future direction in this particular field, structural engineering will be developed from the following aspects.

First, integrating multiple strategies for structural engineering may be a promising approach to maximizing the light absorption, charge separation, and surface catalytic reaction at the same time. For example, the separated redox active sites with a fast charge transfer route can be achieved in Z-scheme system. The enhanced visible-light absorption is usually established by nitrogen doping. Therefore, the integration of these strategies can accomplish high charge separation efficiency, strong redox ability, and visible-light absorption. [466] To maximize photocatalytic performance, combinatory application of various strategies in structure engineering is necessary to deal with each component on surfaces or interfaces. So, one of the biggest challenges in photocatalysts design is to appropriately integrate these strategies.

Second, more in-depth study should be conducted on some promising strategies, such as the polarization regulation, to further disclose the mechanism for charge separation and photocatalytic activity enhancement. In addition, there are also many nature inspired methods to expand the new tactics of structural engineering, such as fabrication of semiconductor biohybrid systems, [467–469] chlorophyll loading, [470,471] or bonding the chromophore, [472] which may attract considerable research interests in the future.

Third, the mechanism of CO₂ reduction has been illustrated in a large number of works by in situ techniques, such as in situ IR and Raman. [473] Using new strategies to design semiconductors usually realized enhanced catalytic activity with diverse final products. But the mechanism behind these results is still unclear and under debate. More attentions should be paid to the changing of key intermediates and reaction pathways, because diverse active sites are built on semiconductor by various strategies. More in situ techniques are required to identify reaction pathways on the specific structure. The mechanism for exact reaction pathways may differ from the currently recognized one, which can advance the development of CO₂ photoreduction.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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Shuobo Wang received his Ph.D. degree in materials science and technology, China University of Geosciences (Beijing), in 2020. His research interests focus on the design and synthesis of photocatalysts for the applications in CO2 reduction and environmental remediation.

Xu Han received B.S. degree in materials science and technology, China University of Geosciences (Beijing), in 2014. She is currently a Ph.D. candidate in the School of Materials Science and Technology, China University of Geosciences (Beijing). Her research interests focus on the design and synthesis of bismuth-rich bismuth oxyhalides photocatalysts, and their applications for environment.

Yihe Zhang received his Ph.D. from Technical Institute of Physics and Chemistry, Chinese Academy of Sciences in 2005, and undertook a visiting scholar, postdoctoral fellow, and research fellow in City University of Hong Kong and The Hong Polytechnic University from 2003 to 2009. He is a professor at School of Materials Science and Technology, China University of Geosciences (Beijing) and leads the Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, School of Materials Science and Technology, China University of Geosciences (Beijing). His current research focuses on nanomaterials, composites and their applications for environment and energy.
Na Tian is a lecturer at the Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, School of Materials Science and Technology, China University of Geosciences (Beijing). She received her Ph.D., in 2018, from the School of Materials Science and Technology, China University of Geosciences (Beijing). Her research focuses on the design and synthesis of photocatalysts for environmental purification, photocatalytic H₂ generation and CO₂ reduction.

Tianyi Ma received his Ph.D. in physical chemistry in 2013 from Nankai University, China. He then worked as a postdoctoral research fellow from 2013 to 2014 at University of Adelaide, Australia. He is currently a senior lecturer in Discipline of Chemistry at University of Newcastle, leading an independent research group focusing on energy materials and catalysis.

Hongwei Huang is a professor at Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, School of Materials Science and Technology, China University of Geosciences (Beijing). He received his Ph.D., in 2012, from Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, and worked as a visiting scholar in the labs of Prof. Thomas Mallouk in The Pennsylvania State University (2016-2017). His current research mainly focuses on the crystal structural design and charge regulation of layered photocatalytic nanomaterials and their applications for environment and energy.