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# Recent advances in interface engineering of bismuth-based materials for photocatalytic CO<sub>2</sub> reduction

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Photocatalytic reduction of CO<sub>2</sub> into value-added products is witnessed as a promising technology to mitigate global warming and energy crisis. Among the illustrious functional semiconductors, bismuth-based materials are feasible for the CO<sub>2</sub> reduction reaction owing to their convenient preparation, their narrow band gap and the availability of hybridized energy states in the conduction band. Furthermore, the inherent two dimensional (2D) layered structure of few Bi materials remains an added advantage for various photocatalytic reactions. In this focused review, the interfacial engineering of Bi-based semiconductors achieved by coupling them with distinct photocatalytic materials to form type-I, type-II, Z-scheme or S-scheme heterojunctions is discussed, and their applications in CO<sub>2</sub> reduction reactions are emphasized. Further advancements, including co-catalyst loading, defect engineering and designing hierarchical morphology from the perspective of improving charge carrier separation and structural stability are highlighted. The preparation methods and mechanistic pathways for the CO<sub>2</sub> reduction reaction are briefly summarized. Finally, the challenges and scope of Bi-based materials to spotlight their applications in energy- and environment-related areas are presented.

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## 1 Introduction

Global energy consumption using nonrenewable fossil fuels has skyrocketed in the recent decade, leading to significant global climate changes and an imbalance in the ecosystem. As per the literature, CO<sub>2</sub> emissions have substantially increased by ~40% since the industrial revolution.<sup>1,2</sup> Therefore, the development of efficient methods to convert CO<sub>2</sub> into value-added products has drawn attention because they can conveniently address environmental issues and energy demands.<sup>3</sup> Numerous technologies such as chemical reforming, biological, electrochemical, photocatalytic, and photoelectrocatalytic processes have been extensively investigated over the years to address these issues.<sup>4–9</sup> Among them, photocatalytic CO<sub>2</sub> reduction is found to be a sustainable solution for the removal of atmospheric CO<sub>2</sub> and its transformation into selective gaseous (methane or ethane) and liquid-phase products (formate, methanol, or ethanol) are interesting.<sup>10–12</sup> Compared to other approaches, this technique benefits from superior product selectivity, economic viability and environmental benignness.<sup>13</sup> Linear CO<sub>2</sub> with sp<sup>2</sup> hybridized C=O bonds requires more dissociation energy than C–C and C–H bonds, and an adequate amount of energy is required to activate CO<sub>2</sub> molecules.<sup>14,15</sup> The primary step in

the reduction process demands the strong adsorption of CO<sub>2</sub> on the catalytic surface, which is subsequently followed by its activation by surface active sites.<sup>16–18</sup> CO<sub>2</sub> photoreduction imitates the photosynthesis of plants, *i.e.*, it utilizes water and CO<sub>2</sub> and converts them into chemical fuels such as methane or methanol and value-added multi-carbon products. The reaction product ratio varies with the number of electrons participating in the reaction, nature of photocatalytic materials and the adopted reaction conditions.<sup>14–18</sup>

The primary step in semiconductor photocatalysis involves the absorption of light energy by catalysts with energy levels greater than or equal to those of their band gaps to generate electron–hole pairs. These excitons migrate towards the surface and interact with the adsorbed species to produce products *via* redox reactions, which later desorb from the surface of the catalyst.<sup>19</sup> As per theoretical calculations and kinetic studies, CO, COOH and COH are common intermediates in the CO<sub>2</sub> reduction reaction.<sup>20</sup> CO<sub>2</sub> photoreduction will proceed only when the energy of the conduction band of the concerned semiconductor is more negative than the reduction potential of the desired products.<sup>2</sup> Semiconductors such as BiOX, CdS, g-C<sub>3</sub>N<sub>4</sub>, Cu<sub>2</sub>O, SnO<sub>2</sub>, TiO<sub>2</sub>, ZnO, and perovskites are extensively used for the CO<sub>2</sub> reduction reaction.<sup>21–31</sup> Bismuth-based materials have garnered major interest because they possess band gaps spanning the major portion of the solar spectrum, and their band edge positions are convenient to trigger the desired

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reduction and oxidation reactions.<sup>32–37</sup> The Bi 6s orbital hybridizes with the O 2s orbital to form a highly dispersive energy band structure, which promotes charge carrier transport and also exhibits high oxidizing capabilities. Furthermore, bismuth-based materials offer stable structures with layered spaces to promote the intercalation of foreign ions without changing their structural features. Because of their low toxicity, environmental friendliness and exceptional photostability, the distinct morphologies of bismuth-based materials have been explored for photocatalytic applications.<sup>11,38</sup> Different categories of bismuth-based materials such as unitary (Bi), binary ( $\text{Bi}_2\text{S}_3$  and  $\text{Bi}_2\text{O}_3$ ), and ternary (stoichiometric and non-stoichiometric bismuth oxyhalides,  $\text{BiVO}_4$ ,  $\text{Bi}_2\text{WO}_6$ , and  $\text{Bi}_2\text{MoO}_6$ ) are used for photocatalytic  $\text{CO}_2$  reduction.<sup>36,39–41</sup> However, the massive charge carrier recombination and narrow optical response of single-phase photocatalysts limit their performance under light-illuminated conditions.<sup>39,42,43</sup> Several reviews on bismuth-based materials for photocatalytic applications can be found in the literature.<sup>37,38,41,44,45</sup> However, the recent trend in the interfacial engineering of these materials is scarcely emphasized. Motivated by these aspects, this review summarizes the interfacial engineering of bismuth-based materials with various semiconductors under different reaction conditions, and their performance in photocatalytic  $\text{CO}_2$  reduction is outlined.

## 2 Strategies for interfacial engineering

Heterojunction formation is found to be a promising method to improve the photocatalytic performance of semiconductors owing to the synergistic interactions arising from the structure–optical–morphological properties of the integrated semiconductors.<sup>46–49</sup> The prime requisite to fabricate a heterojunction is that the band position of the concerned semiconductors must possess different potentials to achieve the maximum separation of charge carriers.<sup>50,51</sup> Secondly, the bandgap response of the individual components must be substantially different so that the composite absorbs a larger fraction of the solar light for the photocatalytic reactions. Various types of heterojunctions have been fabricated for bismuth-based materials to increase the conversion efficiency of  $\text{CO}_2$  to value-added products. Following are the methods that have been adopted extensively for various types of bismuth-based materials:

(i) Type-II heterojunction: when two semiconductors with different band edge potentials and Fermi levels encounter each other, three types of heterojunctions, namely, type-I, type-II and type-III, are formed. Type-I allows for the migration of both the charge carriers from one semiconductor to another due to their straddle bandgap configuration, which enhances charge carrier recombination (Fig. 1). In contrast, type-II is efficient in separating the electron–hole pairs due to the staggered configuration of the electronic band positions. It is also referred to as the cascade electron transfer process, as it promotes interfacial charge

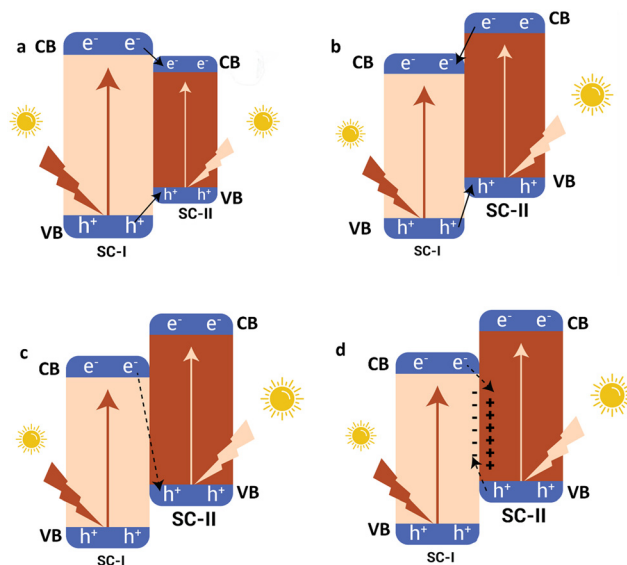


Fig. 1 Different types of semiconductor–semiconductor heterojunctions: a) type-I, b) type-II, c) Z-scheme, and d) S-scheme heterojunctions. Note: SC = semiconductor; CB = conduction band; VB = valence band.

carrier separation. However, the potential of electrons and holes decreases, lowering the efficiency of the composite.

(ii) Z-scheme: though type-II heterojunctions can improve the photocatalytic activity, they suffer from the recombination of electrons and holes. This disadvantage can be avoided by the Z-scheme technique.<sup>52</sup>

The band gap configuration in the Z-scheme is similar to the type-II configuration, but an exception remains in the direction of electron transfer pathways. The low-potential electrons accumulated on one side of the semiconductor recombine with the low-potential holes of another semiconductor, thereby retaining the high-potential electrons and holes for the redox reactions.

Although significant improvement can be observed from Z-scheme photocatalysis, this technique fails to deliver superior photocatalytic performance as the limitation arises from the choice of the semiconductors.<sup>53</sup>

(iii) S-scheme heterojunction: the step scheme (S-scheme) was introduced by the Jiaguo Yu group.<sup>54,55</sup> When reduction and oxidation photocatalysts are in close contact, the electrons in the oxidation photocatalyst recombine with holes present in the valence band of the reduction photocatalyst. Positive and negative charges are formed at reduction and oxidation photocatalysts, respectively, and the direction of the in-built electric field is from the reduction photocatalyst to the oxidation photocatalyst. Thus, electron depletion at the reduction photocatalyst causes the upward band bending, and electron accumulation at the oxidation photocatalyst results in the downward band bending. Driven by the rise of the electric field and Coulombic force of attraction, the electrons in the oxidation photocatalyst recombine with holes in the reduction photocatalyst while preserving the energetic charge carriers for the desired redox reactions.<sup>55</sup> The



preserved electrons and holes are available for the reaction to take place, making the photocatalytic system more efficient than type-II and Z-scheme heterojunctions. The positions of the conduction and valence bands for different bismuth-based materials clearly signify their ability to participate in the CO<sub>2</sub> reduction reactions (Fig. 2).

(iv) Cocatalyst loading: cocatalysts such as noble metals, which include Pt, Ag and Au, non-noble metals, such as Bi, Cu, and Mg, have been exploited to improve the performance of the photocatalytic process.<sup>56–58</sup> The activation energy required to convert CO<sub>2</sub> to any value-added product can be reduced by the addition of cocatalysts on the semiconductor surface. It is also found from the literature that it increases reaction sites and plays a vital role in determining the selectivity, adsorption of CO<sub>2</sub>, and photostability of the photocatalyst.<sup>59,60</sup>

(v) Defect engineering: defects are of paramount importance in tailoring the bandgap and charge carrier dynamics of functional semiconductors. In general, anionic vacancies like oxygen vacancies can narrow the gap region and shift the optical response of the host matrix to the visible region. Few reports also hint that the tailoring the bandgap depends on the density of oxygen vacancies in the host matrix.<sup>61,62</sup> Furthermore, oxygen vacancies can trap charge carriers to restrain their recombination with holes and extend the charge carrier lifetime. On the contrary, cationic vacancies can temporarily trap holes. In recent times, the vacancy-rich Bi-based materials are reported to show superior photocatalytic activity compared to their low-defect counterparts.<sup>45,63,64</sup> These defects can alter lattice strain and surface defects, which can facilitate the adsorption of oxygen to promote the formation of superoxide radicals in the solution phase.<sup>65</sup>

## 3 Bi-based semiconductors

### 3.1 BiOX

BiOX is highly crystalline with a tetragonal crystal structure and is extensively used for photocatalytic applications owing

to its layered structure and narrow band gap.<sup>66</sup> It is composed of a layered structure with [Bi<sub>2</sub>O<sub>2</sub>] slabs and two arrays of [X]<sup>−</sup> ions. The exciton pairs can be effectively separated because the charge density is higher in Bi–O than in [X] slabs. In addition, the static electric field along the *c*-axis avoids massive charge carrier recombination pathways.<sup>67</sup> BiOCl is an indirect band gap semiconductor, which decreases the chance of the recombination of charge carriers.<sup>68–71</sup> Defects in BiOX can influence the photocatalytic activity by modifying the charge transport and electronic structure of the material. The oxygen vacancy can be introduced easily to BiOCl because the Bi–O bond is weak. These oxygen vacancies can increase the number of active sites to facilitate the CO<sub>2</sub> adsorption and activation processes.<sup>72</sup> It has been observed that the majority of BiOX-based heterojunctions produce only CO and CH<sub>4</sub>, and therefore, the interfacial engineering of BiOX plays a crucial role in improving the selectivity.<sup>73</sup> The crystal facet of BiOCl also influences the photocatalytic activity when coupled with CdS. CdS/BiOCl with an exposed {001} facet exhibited higher performance than {010} facets.<sup>67</sup> This was attributed to the effective coupling of the interfacial electric field of the heterojunction and the polarization electric field of the {001} crystal facet of BiOCl. The production of CH<sub>4</sub> and CO with {001}-BiOCl/CdS was higher than that with {010}-BiOCl/CdS, even though the bandgap energy and band edge potential of both the facets were almost similar. This result suggests that the crystal facet orientation of BiOCl has a profound influence on the adsorption and activation of CO<sub>2</sub>. As the polarization electric field for BiOCl is along the *c*-axis, excited electrons easily accumulate on the {001} facet, which favours their recombination with the valence band holes of CdS, thereby improving the energetic electrons and holes from CdS and BiOCl, respectively, to participate in the redox reactions.<sup>67</sup> The 2D/2D Vo–WO<sub>x</sub>/BiOCl S-scheme was fabricated by a self-assembly process. The S-scheme heterojunction not only offered the separation of photogenerated charge carriers but also provided a dual interfacial pathway to improve the charge separation

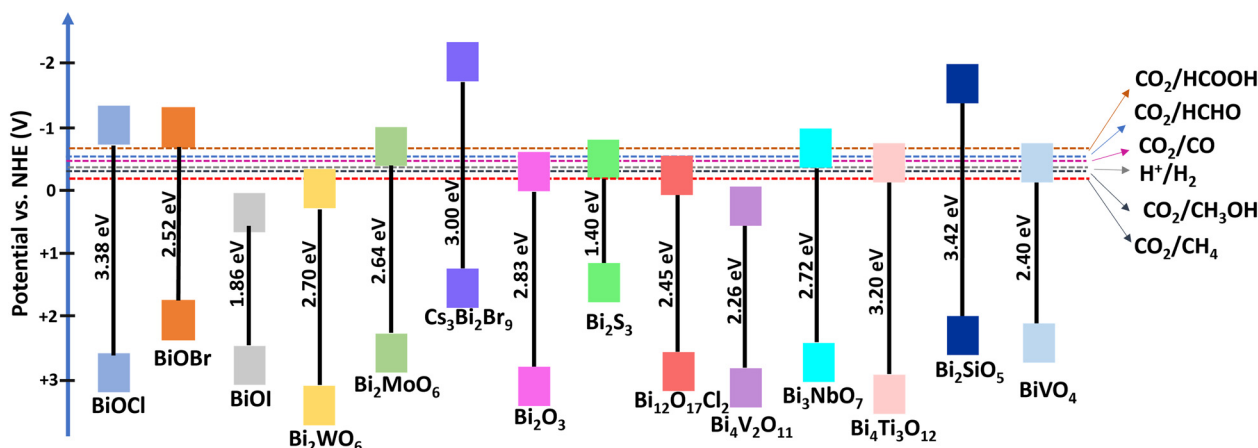


Fig. 2 Band positions of different bismuth-based semiconductors.



process.<sup>74</sup> Jiang *et al.* showed that CO<sub>2</sub> molecules were adsorbed on BiOCl (001) and WO<sub>x</sub> (010) surfaces.<sup>75</sup> The study also suggested that CO<sub>2</sub> molecules were more stable on the surface of BiOCl than that of WO<sub>x</sub>. The conduction band level of WO<sub>x</sub> was not sufficient to carry out the reduction of CO<sub>2</sub> molecules. As a result, the adsorption and reaction sites were available only on the surface of BiOCl.<sup>75</sup> Similarly, Bi<sub>2</sub>WO<sub>6</sub> was also used to fabricate a heterojunction with BiOCl. Unlike the S-scheme in WO<sub>x</sub>/BiOCl, they formed a typical type-II heterojunction. Theoretical calculations confirmed that the production of the CHO\* intermediate on the surface of BiOCl/Bi<sub>2</sub>WO<sub>6</sub> was responsible for the selective generation of CH<sub>4</sub>. The high selectivity towards CH<sub>4</sub> was due to the ultrathin nanosheet morphology (2D/2D) and the presence of an internal electric field at the heterointerface.<sup>76</sup> BiOCl/In<sub>2</sub>O<sub>3</sub> fabricated by the hydrothermal method with a type-II heterojunction yielded a high rate of CO<sub>2</sub> photoreduction.<sup>77</sup> This enhanced performance was attributed to the narrow band gap, which falls in the visible region. In another report, a chlorophyll and Mg co-modified BiOCl (Chl-Mg/BiOCl) microsphere exhibited superior photocatalytic applications. Chl-Mg/BiOCl yielded 100 μmol g<sup>-1</sup> of CH<sub>4</sub>. The chlorophyll

on the surface of the BiOCl produced singlet states of Chl-Mg\*, which acted as an electron donor. Mg formed a complex with chlorophyll and helped to improve the stability of the catalyst.<sup>78</sup>

It is also noted that the cocatalyst loading on the photocatalyst is a potential approach to improve the adsorption of the intermediates during CO<sub>2</sub> reduction, thereby influencing the coupling of the C-C bond. To improve C<sub>2</sub> hydrocarbon selectivity and to enhance the photocatalytic reduction of CO<sub>2</sub>, transition metal cocatalysts with nanostructures were loaded on BiOCl.<sup>71,79,80</sup> The selectivity towards CH<sub>4</sub> was increased by decorating noble metals, such as Pd, on BiOCl. Pd not only decreased the recombination of the charge carriers but also changed the intermediate formed (from HCO<sub>3</sub><sup>-</sup> to HCOO\* and CH<sub>3</sub>O\*; CH<sub>3</sub>O\* will be reduced to CH<sub>4</sub>) on the surface of BiOCl.<sup>80</sup>

*In situ* diffused reflectance infrared Fourier transform (DRIFT) spectroscopy revealed that the key intermediates were bidentate formate and methoxy, which promote the selectivity for CH<sub>4</sub> production.<sup>80</sup> The photocatalytic activity of ultrathin BiOCl sheets can be altered by introducing magnetically active metal particles. In this context, Li *et al.*

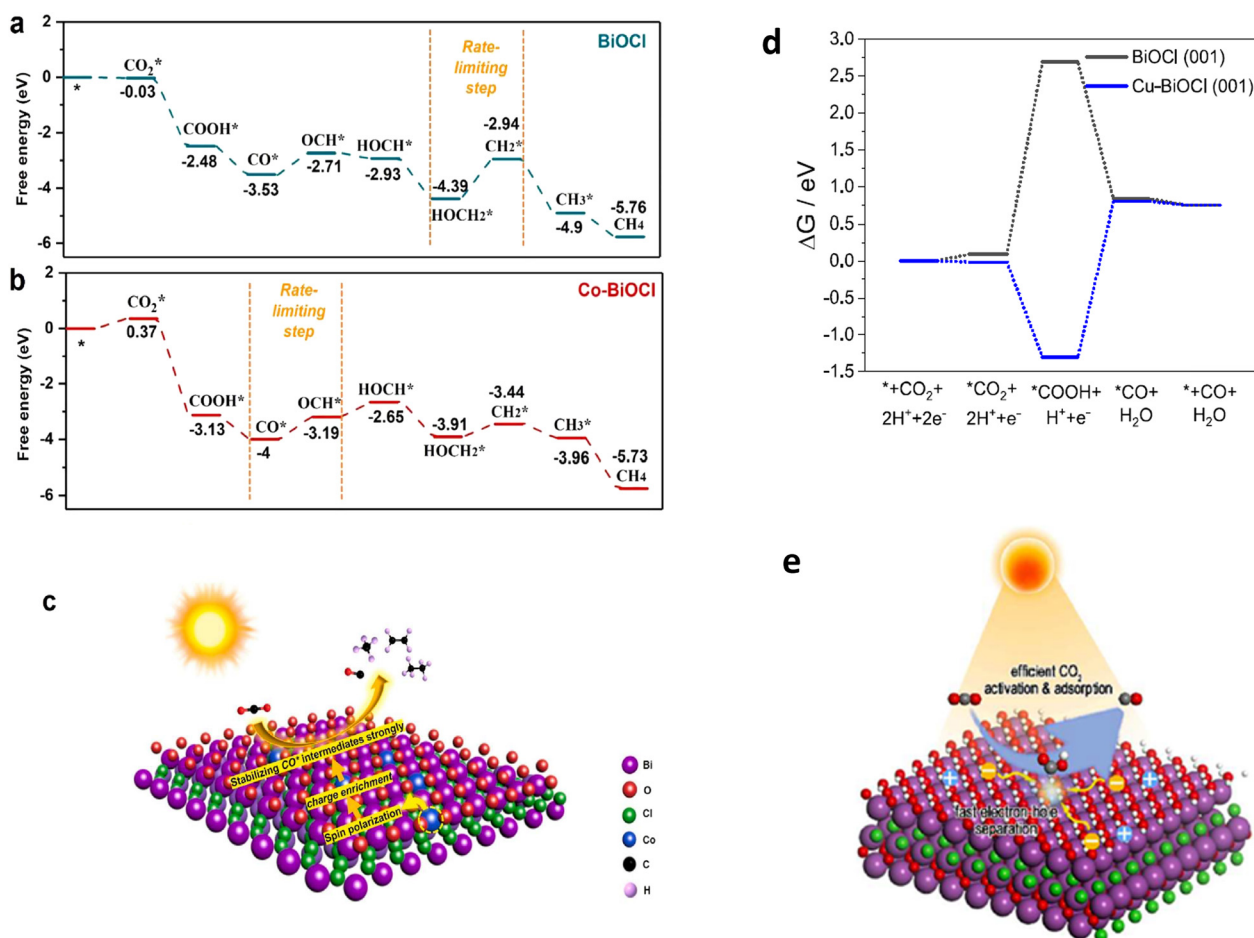


Fig. 3 Computed Gibbs free energy main reactions for the photocatalytic reduction of CO<sub>2</sub> on a) pristine BiOCl and b) Co-BiOCl.<sup>79</sup> c) CO<sub>2</sub> reduction pathway on the surface of Co-BiOCl. d) Gibbs free energy diagram for CO<sub>2</sub> reduction on Cu-BiOCl. e) Scheme for the photoreduction of CO<sub>2</sub> to CO. Reproduced with permission from ref. 68. Copyright 2022, American Chemical Society and ref. 79. Copyright 2024, Elsevier.



reported that Co-doped BiOCl selectively converted CO<sub>2</sub> to CH<sub>4</sub> and C<sub>2+</sub> products, which was not possible with the pristine BiOCl. The increase in the photocatalytic activity was due to the Co–O bond on the Co–BiOCl.<sup>79</sup> The increased CO<sub>2</sub> adsorption was primarily responsible for the enhanced CO<sub>2</sub> photoreduction. It was also found that the introduction of Co on BiOCl generated spin-polarized charges and changed the intermediate formed on the surface of BiOCl. In order to generate CH<sub>4</sub> and C<sub>2+</sub> products, the CO\* intermediate would be formed *via* the formation of the COOH\* intermediate (Fig. 3a–c). The rate-limiting step for Co–BiOCl was the conversion of CO\* to CHO\*, whereas for BiOCl, HOCH<sub>2</sub>\* to CH<sub>2</sub>\* was the rate-limiting step.<sup>79</sup> This work showed that the spin polarization of the charge on the surface of BiOCl resulted in the formation of a stable intermediate and promoted C–C coupling to yield CH<sub>4</sub> and C<sub>2+</sub> products. Similarly, Cu was modified on BiOCl nanosheets, which resulted in surface charge distribution. Cu–BiOCl improved the catalytic performance and enhanced the absorption of light.<sup>71</sup> Also, it decreased the activation energy barrier, which facilitates the faster consumption of CO<sub>2</sub> molecules, resulting in an increased CO yield (Fig. 3d and e). Metal cocatalysts, such as Pt, Pd and Au metals, have been decorated on BiOCl nanostructures by the deposition–precipitation method. The main product obtained with BiOCl was CO, while CH<sub>4</sub> production dominated after loading the metal cocatalyst.<sup>81</sup>

Chen *et al.* demonstrated that Z-scheme In<sub>2</sub>S<sub>3</sub>/BiOCl could be prepared by solution combustion synthesis. The nanopetals of BiOCl were decorated on the nanoflowers of In<sub>2</sub>S<sub>3</sub> *via* solution combustion synthesis. In<sub>2</sub>S<sub>3</sub>/BiOCl nanostructures were evenly deposited on the surface of MnO<sub>2</sub> nanowires.<sup>82</sup> Initially, In<sub>2</sub>S<sub>3</sub> nanoflowers were synthesized by the hydrothermal approach. The synthesized In<sub>2</sub>S<sub>3</sub> nanoflowers were dissolved in thiourea, a bismuth nitrate precursor and concentrated nitric acid and stirred vigorously. To this solution, urea and ammonium chloride were added and stirred constantly for 24 h. The In<sub>2</sub>S<sub>3</sub>/MnO<sub>2</sub>/BiOCl was fabricated by using the suspension of In<sub>2</sub>S<sub>3</sub>/BiOCl by the hydrothermal approach. Despite having higher solubility than In<sub>2</sub>S<sub>3</sub>, BiOCl grew on the surface of In<sub>2</sub>S<sub>3</sub>.<sup>82</sup> In<sub>2</sub>S<sub>3</sub>/BiOCl deposited uniformly on MnO<sub>2</sub> nanowires, which formed an assembly of hierarchical structures. It is noted from this work that the S<sup>2-</sup> ions play a significant role in controlling the nucleation of In<sub>2</sub>S<sub>3</sub>, forming the morphology and controlling the size of the nanostructure. This ternary heterojunction exhibited photocatalytic reduction rates of 51.2 μmol g<sup>-1</sup> h<sup>-1</sup> for CO<sub>2</sub> to CO, 63.2 μmol g<sup>-1</sup> h<sup>-1</sup> for CO<sub>2</sub> to C<sub>2</sub>H<sub>4</sub>, and 42.4 μmol g<sup>-1</sup> h<sup>-1</sup> for CO<sub>2</sub> to CH<sub>4</sub> conversion.<sup>82</sup> The observed synergistic effect was attributed to the Mn 3d electrons, which have narrowed the band gap. The key intermediates of the photocatalytic reduction were CHO\* and COOH\* for the production of CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>.<sup>83</sup> BiOCl with a BiOBr heterojunction was fabricated by the

mechanical method, which yielded the type-I heterojunction.<sup>84</sup> This heterojunction reduced CO<sub>2</sub> to CO with a formation rate of 7.353 μmol g<sup>-1</sup> h<sup>-1</sup>.

The CsPbBr<sub>3</sub> perovskite is attracting increasing attention owing to its visible light harvesting capability, and its high conduction band position enhances the reduction capability.<sup>85</sup> Various heterojunctions have been constructed based on the CsPbBr<sub>3</sub> perovskite because the pristine material suffers from severe recombination of charge carriers. A 2D/2D S-scheme heterojunction comprising BiOCl and CsPbBr<sub>3</sub> was fabricated by an efficient self-assembly method. The zeta potential measurements revealed the negative and positive surface charge densities on BiOCl and CsPbBr<sub>3</sub>, which could adhere to each other *via* electrostatic forces of attraction. The nanosheets of the perovskite were assembled on the nanosheets of BiOCl, which provided face-to-face contact, and a strong interfacial area existed between them. This heterojunction afforded much improved photocatalytic activity towards CO<sub>2</sub> reduction to form CO as the major product and CH<sub>4</sub> as a minor product.<sup>85</sup> The high content of CsPbBr<sub>3</sub> in the composite reduced the CO production, while the yield of CH<sub>4</sub> remained almost the same irrespective of its content.<sup>85</sup>

Chen *et al.* synthesized BiOCl by the hydrothermal method, and the oxygen vacancy was introduced by heating at 60 °C in a vacuum oven.<sup>86</sup> The Z-scheme heterostructure was fabricated by vigorously stirring powders of BiOCl with oxygen vacancies and 2D g-C<sub>3</sub>N<sub>4</sub> nanosheets in an ultrasonic bath. It was found that the heterojunction could be constructed effectively if the two individual components were stirred in an ultrasonic bath rather than on a magnetic stirrer.<sup>86</sup> The authors observed that the photocatalytic reduction of CO<sub>2</sub> to CO on the interfacial oxygen-vacancy induced g-C<sub>3</sub>N<sub>4</sub>/BiOCl heterostructure was 1.6 times higher than that on the pristine g-C<sub>3</sub>N<sub>4</sub>/BiOCl.

Ternary composites of BiOCl with dual Z-schemes of BiOCl/g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>2</sub>CrO<sub>4</sub> have also been synthesized and found to give CO and CH<sub>4</sub> with yields of 30.20 and 81.21 μmol g<sup>-1</sup>, respectively.<sup>87</sup> It is possible to make a ternary heterojunction with C<sub>3</sub>N<sub>4</sub> and BiOCl using the Ag<sub>2</sub>CrO<sub>4</sub> photocatalyst. The dual Z-scheme heterojunction photocatalyst was synthesized by a simple method. BiOCl/C<sub>3</sub>N<sub>4</sub> was prepared by taking the Bi, C and N precursors and heating solvothermally using ethylene glycol as the solvent for 12 h at 140 °C. However, the BiOCl/C<sub>3</sub>N<sub>4</sub>/Ag<sub>2</sub>CrO<sub>4</sub> was synthesized by stirring the powders of BiOCl/C<sub>3</sub>N<sub>4</sub> and precursors of Ag<sup>+</sup> and Cr<sup>6+</sup> ions for 2 h. When the ternary heterojunction was formed, the morphologies of BiOCl, C<sub>3</sub>N<sub>4</sub> and Ag<sub>2</sub>CrO<sub>4</sub> were retained. The irregular shapes of Ag<sub>2</sub>CrO<sub>4</sub> were uniformly decorated on the microspheres of BiOCl and the nanosheets of C<sub>3</sub>N<sub>4</sub>. It was observed that C<sub>3</sub>N<sub>4</sub> provided charge transfer pathways to form dual Z-scheme heterojunctions.

MgIn<sub>2</sub>S<sub>4</sub> is another chalcogenide that exhibits a promising band gap and photostability and is extensively used for the removal of liquid pollutants and for the production of



hydrogen.<sup>88</sup> Zhang *et al.* fabricated an S-scheme heterojunction of Bi–BiOCl/MgIn<sub>2</sub>S<sub>4</sub> by the hydrothermal technique and NaBH<sub>4</sub> reduction technique.<sup>89</sup> The microspheres of BiOCl with an average diameter of 1 μm were obtained by the hydrothermal method, and Bi self-doped BiOCl was synthesized by treating BiOCl microspheres with NaBH<sub>4</sub>, followed by vacuum drying. Bi–BiOCl/MgIn<sub>2</sub>S<sub>4</sub> was synthesized by the *in situ* hydrothermal method, and the obtained product exhibited ultrathin sheets of BiOCl dispersed on the surface of MgIn<sub>2</sub>S<sub>4</sub> marigold flowers. It was noted that NaBH<sub>4</sub>, which was used as a reducing agent, influenced the morphology of BiOCl and caused the rough surfaces and loose internal structures.<sup>89</sup> The formed S-scheme heterojunction exhibited the conversion of CO<sub>2</sub> to CH<sub>4</sub> with a yield of 25.72 μmol g<sup>-1</sup>.

BiOBr exhibits an appropriate band structure, making it suitable for photocatalytic applications. However, the performance of BiOBr needs band-structure modification, as it promotes electron–hole recombination. The g-C<sub>3</sub>N<sub>4</sub> has a band gap that falls in the visible light wavelength, and therefore, coupling it with BiOBr would help utilize a larger fraction of solar light.<sup>90</sup> The hollow microspherical morphology of BiOBr

was completely destroyed when grown on the surface of g-C<sub>3</sub>N<sub>4</sub> sheets *via* the wet-chemical approach. The composite selectively produced CH<sub>3</sub>OH from CO<sub>2</sub> at the optimized content of g-C<sub>3</sub>N<sub>4</sub>.<sup>90</sup> Liu *et al.* synthesized BiOBr/C<sub>3</sub>N<sub>4</sub> by ultrasonically synthesizing the synthesized BiOBr and C<sub>3</sub>N<sub>4</sub> for 6 h.<sup>91</sup> BiOBr was synthesized by the solvothermal technique, and the oxygen vacancy was introduced by adding the surfactant along with precursors. Furthermore, oxygen vacancies could be introduced to BiOBr by adding the surfactant during solvothermal synthesis, which is not possible during hydrothermal synthesis. The g-C<sub>3</sub>N<sub>4</sub> heterojunction was constructed with BiOBr possessing surface oxygen vacancies. The morphology has been compared in Fig. 4.<sup>91</sup> Along with the heterojunction interface, the presence of surface oxygen vacancies promoted the charge separation, and hence, the photocatalytic performance was enhanced.

Xi *et al.* also synthesized BiOBr/Bi<sub>2</sub>S<sub>3</sub> and conducted a detailed analysis on the growth mechanism of Bi<sub>2</sub>S<sub>3</sub> nanoarrays on BiOBr nanoplates.<sup>92</sup> The facet-sensitive growth of Bi<sub>2</sub>S<sub>3</sub> can be used as an effective strategy to construct a heterojunction with an increased number of active sites using thioacetamide as the sulfur source. It can also be observed

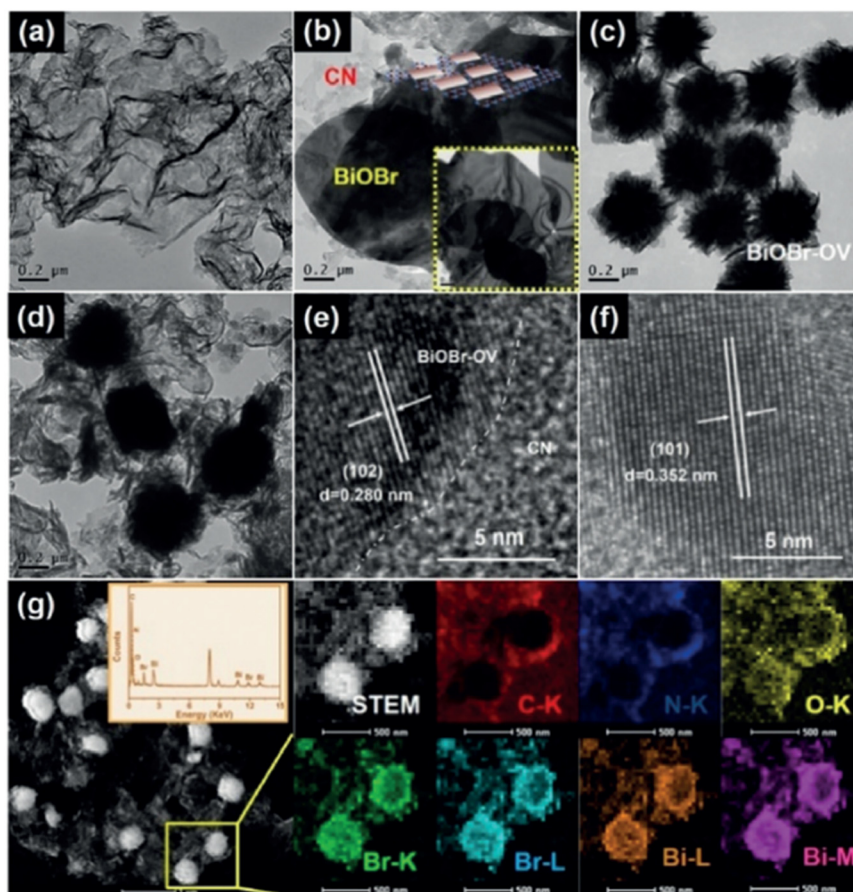


Fig. 4 Transmission electron microscopy (TEM) images of a) pure C<sub>3</sub>N<sub>4</sub> (CN), b) CN–BiOBr and BiOBr (marked in the lower right corner), c) bare BiOBr–OV, and d) the CN–BiOBr–OV catalyst. e) and f) High resolution (HR)-TEM images of the CN–BiOBr–O<sub>v</sub> heterojunction with the lattice spacings, and g) elemental maps of C, N, O, Br, and Bi in the CN BiOBr–O<sub>v</sub> photocatalyst. Reproduced with permission from ref. 91. Copyright 2020, Wiley-VCH.



that the structurally a very close matching of the lattice parameters between *c*-axis of Bi<sub>2</sub>S<sub>3</sub> and *a* or *b* axis of BiOBr facilitates the selective growth of Bi<sub>2</sub>S<sub>3</sub> facets.<sup>92</sup> The established S-scheme heterointerface between BiOBr and Bi<sub>2</sub>S<sub>3</sub> produced 20.32 μmol g<sup>-1</sup> CO from CO<sub>2</sub> photoreduction.<sup>92</sup> The large area exposure of both semiconductors helped in exploiting the maximum amount of visible light. Directional growth of mesh like Bi<sub>2</sub>S<sub>3</sub> nanostructure as grown on the surface of BiOBr nanoplates *via* topotactic transformation process found to be effective in enhancing the photocatalytic activity.<sup>92</sup>

Vertically aligned Bi<sub>2</sub>S<sub>3</sub> nanowalls helped in the minimal shielding of the light falling on the surface of the BiOBr nanoplate substrate, which extended the optical response to 1000 nm (Fig. 5). The authors demonstrated that the vacancy-rich BiOBr substrate enhanced the adsorption of CO<sub>2</sub> on the surface.<sup>92</sup> Due to the weak Bi-O linkage, it was easy to produce oxygen vacancies in BiOBr. Because oxygen vacancies created trap centres for photogenerated charge carriers, it enhanced the separation efficiency. The rational design of oxygen-vacancy rich BiOBr heterojunctions would be beneficial in elevating the photocatalytic CO<sub>2</sub> reduction.

Ma *et al.* suggested that instead of constructing conventional heterostructures, co-sharing atoms can be an effective strategy for interfacial engineering along with a suitable band structure. This work stresses the atom-level interfacial contact of the heterostructures.<sup>93</sup> BiOBr was coupled with a Bi<sub>2</sub>S<sub>3</sub> layered structure to deliver a full-spectrum responsive S-scheme photocatalyst. BiOBr/Bi<sub>2</sub>S<sub>3</sub> was fabricated by an *in situ* ion exchange method, which yielded Bi<sub>2</sub>S<sub>3</sub> nanorods on BiOBr nanosheets. It was observed that the morphology of BiOBr nanosheets changed after reacting with sulfur atoms during the hydrothermal reaction, which indicates that the occurrence of the ion exchange reaction led to the formation of the heterojunction. It was also noted that as the sulfur concentration increases, the density of Bi<sub>2</sub>S<sub>3</sub> nanorods on BiOBr nanosheets. The BiOBr/Bi<sub>2</sub>S<sub>3</sub> heterostructure yielded 20.32 μmol g<sup>-1</sup> CO.

Bi<sub>2</sub>WO<sub>6</sub> has a layered structure comprising fluorite-like [Bi<sub>2</sub>O<sub>2</sub>]<sup>2+</sup> and perovskite-like [WO<sub>4</sub>]<sup>2-</sup>. Owing to the strong oxidising capability of its valence band, Bi<sub>2</sub>WO<sub>6</sub> is extensively studied for photocatalytic applications. However, the

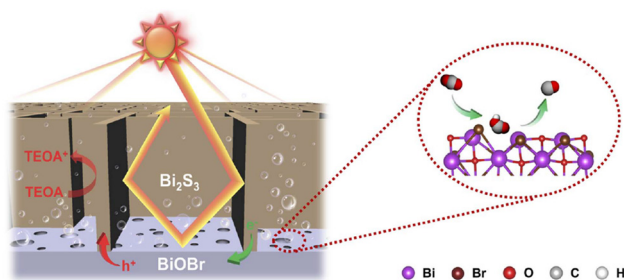


Fig. 5 Schematic illustrating the proposed mechanism for photocatalytic CO<sub>2</sub> reduction over the BiOBr/Bi<sub>2</sub>S<sub>3</sub> heterojunction. Reproduced with permission from ref. 92. Copyright 2022, Royal Society of Chemistry.

performance is limited by the severe recombination of the photogenerated charge carriers. Therefore, a composite of Bi<sub>2</sub>WO<sub>6</sub> and BiOBr would enhance the photocatalytic conversion of CO<sub>2</sub> reduction.<sup>94</sup> It is known from the literature that surface oxygen vacancies can easily be created on Bi<sub>2</sub>WO<sub>6</sub> and BiOBr, which can provide an increased number of adsorption sites for the reactants and trap states for the photogenerated charge carriers.<sup>68,95</sup> Apart from oxides and sulfides, layered double hydroxides (LDHs) have also been used for making composites with BiOBr. CoAl-LDH has high selectivity towards CH<sub>4</sub>, whereas NiAl-LDH yields CO.<sup>96</sup> As CoAl-LDH has suitable band positions with BiOBr, facile electron-hole pair separation is possible. The heterojunction was fabricated by the hydrothermal method. The optimal amount of ultrathin CoAl-LDH loaded on BiOBr improved the selectivity towards CH<sub>4</sub>, a value-added chemical.<sup>96</sup> In most of the cases, pristine BiOBr yields CO *via* photocatalytic conversion. In order to obtain value-added products such as CH<sub>4</sub>, the p-type semiconductor Cu<sub>2</sub>O was heterojunctioned with BiOBr.<sup>97</sup> Recent studies have found that using metallic Bi is beneficial for enhancing the photogenerated charge separation.<sup>14,98,99</sup> Many reports claim that Bi-BiOBr shows enhanced performance towards CO<sub>2</sub> photoreduction.<sup>100</sup> Abundant oxygen vacancies can be successfully synthesized by the *in situ* partial ion-exchange method on the heterojunction materials.<sup>74</sup> More importantly, metallic Bi self-doped Bi<sub>2</sub>SiO<sub>5</sub> synthesized by the hydrothermal method can provide a facile situation for S-scheme heterojunctions and thereby increase the redox capability in the S-scheme BiOBr-(001)/Bi<sub>2</sub>SiO<sub>5</sub>/Bi heterojunction, which gives a CO production rate of 234.05 μmol g<sup>-1</sup> h<sup>-1</sup>.<sup>74</sup>

AgBr is another excellent photo-responsive material, but it suffers from instability due to the reduction of silver ions to metallic silver upon exposure to light. The low electron-hole recombination and extended visible light response were achieved in BiOBr/AgBr.<sup>101</sup> Density functional theory and experimental results demonstrated that an electron depletion region is produced on BiOBr, whereas electrons accumulate on AgBr, resulting in an S-scheme heterojunction to produce CO and CH<sub>4</sub>. As the intensity of the light increases, the production of CO and CH<sub>4</sub> increases linearly, proving that the reaction follows first-order kinetics.<sup>101</sup> BiOBr<sub>x</sub>I<sub>1-x</sub> was coupled with BiPO<sub>4</sub> to form a p-n junction, which was synthesized by the solvothermal method.<sup>102</sup> This heterojunction exhibited increased photocatalytic activity compared to BiPO<sub>4</sub>.<sup>102</sup> The 0D/2D CsPbBr<sub>3</sub>/BiOBr grown under different conditions selectively produced CO rather than CH<sub>4</sub>.<sup>103,104</sup> The oxygen vacancies in BiOBr modulated the adsorption and activation of CO<sub>2</sub>, and the highly negative conduction band position of quantum dots (QDs) promoted the reduction reaction pathways. Recently, the coupling of BiOBr with p-type NiO was reported to be active for CO<sub>2</sub> reduction to yield CO and CH<sub>4</sub>.<sup>105</sup> It was proposed that the adsorption of CO<sub>2</sub> on the composite surface formed carbonate species, which were converted to formic acid by capturing protons and electrons. The formic acid was successively transformed to



formaldehyde, methanol and methane by continuous hydrogenation processes. Alternatively, CO<sub>2</sub> was directly transformed into CO by hydrogenation and dehydration.<sup>105</sup> The conduction band of NiO is mainly derived from the orbitals of Ni, which enables the accumulation of electrons at the Ni sites of NiO, which primarily serve as adsorption centres for CO<sub>2</sub>.<sup>105</sup>

Among BiOX materials, BiOI exhibits the narrowest band gap (~1.6 to 1.9 eV), which enhances the absorption of light in the visible region. BiOI consists of alternative layers of [Bi<sub>2</sub>O<sub>2</sub>] and iodine held by van der Waals forces of attraction. BiOI, an indirect band gap semiconductor, was heterojunctioned with a perovskite material to improve the interfacial charge separation. The direct band gap semiconductor cesium formamidinium lead halide perovskite (Cs<sub>1-x</sub>FA<sub>x</sub>PbBr<sub>3</sub>) was coupled with BiOI nanosheets.<sup>106</sup> It is worth noting that the heterojunction was created by stirring the solution of BiOI and perovskite nanocrystals owing to the low surface energy of perovskite nanocrystals and strong interactions between Bi cations and perovskite Br anion. The perovskite with a cuboid structure was well decorated on the ultrathin nanosheets of BiOI, as confirmed by SEM and TEM images. The authors demonstrated the kinetic models, as shown in Fig. 6, and they claim that BiOI had more surface defects than the perovskite Cs<sub>1-x</sub>FA<sub>x</sub>PbBr<sub>3</sub> (CF).<sup>106</sup> However, when BiOI and CF were heterojunctioned, the blue side of the photoinduced absorption band (PIA) allowed transition with Bi<sup>3+</sup> doping in CF. An internal electric field (IEF) was created due to the electron transfer between BiOI and CF, which facilitates the recombination of electrons from the conduction band of BiOI and the holes from the valence band of the CF perovskite to form an S-scheme heterojunction, as depicted in Fig. 6.

The formation of the S-scheme was confirmed by X-ray photoelectron spectroscopy. Femtosecond transient

absorption spectroscopy was utilized to investigate the ultra-rapid dynamics of charge carriers.

In another work, BiOI nanosheets and In<sub>2</sub>O<sub>3</sub> were synthesized individually by the solvothermal technique.<sup>107</sup> Similar to the above work, a heterojunction was formed by mixing the as-synthesized semiconductors and heating solvothermally to obtain the heterojunction of BiOI/In<sub>2</sub>O<sub>3</sub>. The spherical morphology of In<sub>2</sub>O<sub>3</sub> was decorated on the nanosheets. However, it was observed that the morphology was non-uniform throughout the heterojunction material. It can be inferred that the heterojunction fabricated *via* the solvothermal technique using the individual semiconductor materials resulted in the aggregation of In<sub>2</sub>O<sub>3</sub> on BiOI nanosheets.<sup>107</sup> The BiOI/C<sub>3</sub>N<sub>4</sub> constructed on hydrophobic carbon fiber paper *via* the electrophoretic deposition process exhibited significant selectivity for CO production during the CO<sub>2</sub> reduction reaction.<sup>108</sup> Initially, pre-formed g-C<sub>3</sub>N<sub>4</sub> sheets and an iodine powder were dispersed in the acetone solvent, wherein protons were released upon the reaction of iodine with acetone. Later, BiOI/carbon fibers and Pt electrodes were used as the cathode and anode, respectively, which was followed by the application of an external potential.<sup>108</sup> The BiOI-nanosheets were vertically grown on the surface of carbon fibers, and g-C<sub>3</sub>N<sub>4</sub> sheets completely wrapped the fibers to form 2D/2D contacts between the semiconducting surfaces.<sup>108</sup>

Li *et al.* carried out interfacial engineering with the formation of the p-n junction by compositing BiOI and Zn<sub>2</sub>TiO<sub>4</sub>.<sup>109</sup> The presence of oxygen vacancies sped up the CO<sub>2</sub> reduction process.<sup>110</sup> They extended the lifetime of the charge carrier and also acted as activation sites to enhance the adsorption of CO<sub>2</sub>. Wang *et al.* fabricated a 2D/2D Bi<sub>2</sub>MoO<sub>6</sub>/BiOI S-scheme heterojunction to enhance the photoreduction of CO<sub>2</sub>.<sup>110</sup> BiOI nanosheets were grown on few-layered Bi<sub>2</sub>MoO<sub>6</sub> nanosheets using the solvothermal technique. The S-scheme mechanism was investigated by utilizing time-resolved photoluminescence spectroscopy, work function and charge density difference analyses. The nanosheets of Bi<sub>2</sub>MoO<sub>6</sub> on BiOI nanospheres demonstrated that the van der Waals heterojunction is effective in accelerating the photogenerated charge carriers. The authors established that the charge transfer takes place from Bi<sub>2</sub>MoO<sub>6</sub> to BiOI in addition to large-area van der Waals heterojunctions and S-scheme heterojunctions.<sup>110</sup>

Hongyu Fu *et al.* synthesized the heterostructure of Cu<sub>2</sub>O and carbon-loaded BiOI using two-step methods.<sup>111</sup> The yield of methanol and ethanol from CO<sub>2</sub> was 722.8 μmol g<sup>-1</sup> and 264.46 μmol g<sup>-1</sup> for 8 h respectively. The photocatalytic performance of C-BiOI was significantly increased compared to pristine BiOI. The heterostructure of Cu<sub>2</sub>O and carbon-loaded BiOI further improved the photocatalytic activity. Cu<sub>2</sub>O is a p-type semiconductor with a band gap of 2.2 eV. Nanoparticles of Cu<sub>2</sub>O were decorated onto the nanosheets of C-BiOI by the chemical deposition method. The introduction of Cu<sub>2</sub>O



Fig. 6 (a) Depiction of kinetic models for (a) pristine BiOI and Cs<sub>1-x</sub>FA<sub>x</sub>PbBr<sub>3</sub> (CF) and (b) hybrid Cs<sub>1-x</sub>FA<sub>x</sub>PbBr<sub>3</sub>:BiOI (CF:BiOI) heterojunction samples. IEF represents the internal electric field generated in the heterojunction. Reprinted with permission from ref. 106. Copyright 2022, American Chemical Society.



remarkably increased the photogenerated charge carriers and the surface area of the heterostructure, which provided more active sites for  $\text{CO}_2$  reduction.<sup>111</sup>

$\text{BiOI}$ -based 2D–2D heterojunction materials have been designed in order to elevate the photocatalytic performance. The band structures of  $\text{C}_3\text{N}_4$  and  $\text{BiOI}$  are favourable to form S-heterojunctions, which can boost charge separation.<sup>71</sup> Li *et al.* proposed S-scheme charge transport, which increases the redox capability of both  $\text{BiOI}$  and  $\text{C}_3\text{N}_4$  and converts  $\text{CO}_2$  to  $\text{CO}$ .<sup>112</sup> The formation of the S-scheme heterojunction facilitates the electrons to move from  $\text{C}_3\text{N}_4$  to  $\text{BiOI}$ , creating a depletion region in  $\text{C}_3\text{N}_4$ , whereas electron accumulation occurs in  $\text{BiOI}$ . In order to develop wide-wavelength-responding photocatalysts, the authors interfaced  $\text{In}_2\text{O}_3$  with  $\text{BiOI}$ , because  $\text{In}_2\text{O}_3$  exhibits a band gap of 2.8 eV, which falls in the visible region. It is also known to possess good electronic conductivity and is resistant to corrosion. The

type-II heterojunction was fabricated by the solvothermal method.<sup>107</sup>  $\text{In}_2\text{O}_3/\text{BiOI}$  produced  $\text{CO}$  and  $\text{CH}_4$ .<sup>72</sup>

### 3.2 $\text{BiVO}_4$

As there is a larger difference in the reduction potential for  $\text{CO}_2$  and the conduction band potential of  $\text{BiVO}_4$ , only few studies are available on the use of pure  $\text{BiVO}_4$  in the photocatalytic reduction of  $\text{CO}_2$ . It has been found that  $\text{BiVO}_4$  can selectively convert  $\text{CO}_2$  to ethanol. In order to improve the photocatalytic performance, several strategies have been adopted such as morphological control, doping with metals and defect introduction.<sup>56,113</sup> It is found from the literature that metal nanoparticle deposition can effectively tune the band gap of  $\text{BiVO}_4$  and thereby improve the selectivity and conversion efficiency.<sup>113,114</sup> High-performance  $\text{BiVO}_4$  QDs with Au nanoparticles were fabricated and heterojunctioned with rutile nanorod arrays.<sup>115</sup> The

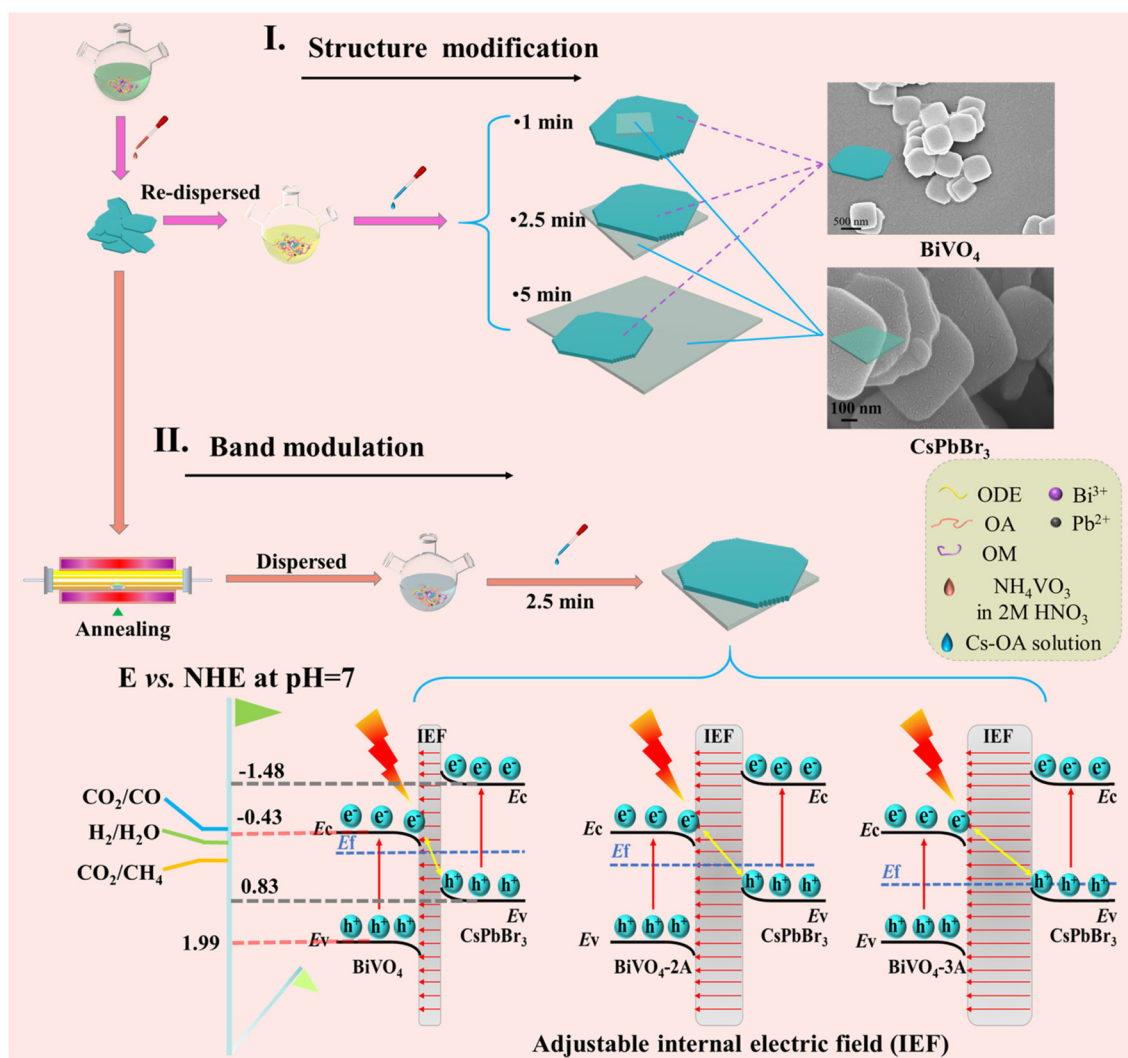


Fig. 7 Schematic of the synthesis, structural modification and band modulation of the  $\text{BiVO}_4/\text{CsPbBr}_3$  heterojunction. Reprinted with permission from ref. 122. Copyright 2022, Elsevier.



surface plasmon resonance of Au not only helped in boosting the charge separation but also increased the light response of the photocatalyst.<sup>116,117</sup> This led to the prolonged lifetime of the charge carriers and the increased separation efficiency. A similar approach was adopted to construct Z-scheme BiVO<sub>4</sub>-Au-Cu<sub>2</sub>O, where BiVO<sub>4</sub> (010)-Au provides the Schottky junction and promotes electron extraction from BiVO<sub>4</sub>.<sup>118</sup> In order to tune the electronic band structure of BiVO<sub>4</sub>, Duan *et al.* co-decorated BiVO<sub>4</sub> with Ag and Bi nanoparticles.<sup>119</sup> The hollow microstructures of Bi/BiVO<sub>4</sub>, which were synthesized by the solvothermal method, showed enhanced performance for the conversion of CO<sub>2</sub> to CO. To further improve photocatalytic reduction towards CO, metallic Ag nanoflakes were loaded on Bi/BiVO<sub>4</sub>. The increased performance was mainly due to the extended visible light response and enhanced separation efficiency. Increased attention has been given to copper to substitute noble metals because it also increases the photocatalytic performance, as copper acts as a hole/electron mediator, which facilitates charge separation and improves the photocatalytic performance.<sup>120</sup> Wei *et al.* fabricated the composites of BiVO<sub>4</sub> and CdS and found an increase in the photocatalytic activity towards CO<sub>2</sub> reduction.<sup>121</sup>

2D-BiVO<sub>4</sub> has also been heterojunctioned with perovskites 2D-CsPbBr<sub>3</sub> to achieve high efficiency in CO formation without any co-catalysts or sacrificial agents (Fig. 7).<sup>122</sup> The preparation step involved the heterogeneous nucleation of CsPbBr<sub>3</sub>-sheets on the surface of BiVO<sub>4</sub> *via* the annealing step in an inert atmosphere, which outlines the stability of BiVO<sub>4</sub> as the substrate surface. The presence of oxygen vacancies in BiVO<sub>4</sub> achieved a gradient Fermi level shift and enlarged the Fermi level gap between the semiconductors. This process was accompanied by an enhanced interfacial electric field in the heterojunction, which consecutively promoted the charge carrier separation process. It is interesting to note that pure CsPbBr<sub>3</sub> had a quasi-square morphology with random sizes, while uniform nanosheets were grown on the BiVO<sub>4</sub> substrate surface, which further emphasize the pivotal role of the

substrate surface in altering the morphological features during the nucleation process.<sup>122</sup>

Wang *et al.* further explored the synthesis of the Bi<sub>2</sub>S<sub>3</sub>/BiVO<sub>4</sub> heterostructure, which was obtained from the *in situ* selective ion exchange method. The authors loaded the cocatalyst MnO<sub>x</sub> on the heterojunction photocatalysts to improve the selectivity.<sup>60</sup> In this work, the photooxidation deposition method was adopted to decorate the MnO<sub>x</sub> facet selectively. BiVO<sub>4</sub> was synthesized by the hydrothermal method, and Bi<sub>2</sub>S<sub>3</sub> nanosheets were preferentially grown on (110) of BiVO<sub>4</sub>. Bi<sub>2</sub>S<sub>3</sub> was grown on (110) of BiVO<sub>4</sub> by sulfurization. As the concentration of S<sup>2-</sup> ions increased, the surface of BiVO<sub>4</sub> turned rough as VO<sup>3-</sup> ions were replaced by S<sup>2-</sup> because the solubility of Bi<sub>2</sub>S<sub>3</sub> was more than BiVO<sub>4</sub>. It is worth noting that if the reaction time was less than 90 minutes, the crystallinity of Bi<sub>2</sub>S<sub>3</sub> was poor and structurally unstable. Therefore, effective interfacial contact would be unsuccessful in the short duration of the reaction.<sup>60</sup> However, as the time duration increased to 120 minutes, the reaction would promote non-selective epitaxial growth. The sponge-like structure of MnO<sub>x</sub> grew selectively on the (110) facets of BiVO<sub>4</sub> rather than on the (010) facets of Bi<sub>2</sub>S<sub>3</sub> nanosheets.<sup>60</sup> The photocatalytic reduction of CO<sub>2</sub> to CH<sub>3</sub>OH was observed in this heterostructure with a production rate of 20 ± 2.33 μmol g<sup>-1</sup> h<sup>-1</sup>.

The type-II heterojunction of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> with BiVO<sub>4</sub> was fabricated through a simple electrospinning technique and a solvothermal method.<sup>123</sup> Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> with BiVO<sub>4</sub> formed a type-II heterojunction, which yielded various intermediates to give CO and CH<sub>4</sub>OH (Fig. 8). A direct S-scheme heterojunction was formed between BiVO<sub>4</sub> and TiO<sub>2</sub>, which changed the charge separation. Platinum decoration was carried out to enhance the CO<sub>2</sub> photoreduction. Platinum decoration on the surface of these catalysts helped in converting CO<sub>2</sub> to CH<sub>4</sub> by mitigating electron-hole pair recombination.<sup>124</sup>

An S-scheme heterojunction was fabricated by growing BiVO<sub>4</sub> on the surface of a metal-organic framework PCN-224 (Cu).<sup>125</sup> This photocatalyst exhibited 100% CO selectivity. Liu *et al.* decorated Co-Pi, a cocatalyst, on BiVO<sub>4</sub>/SnO<sub>2</sub> and

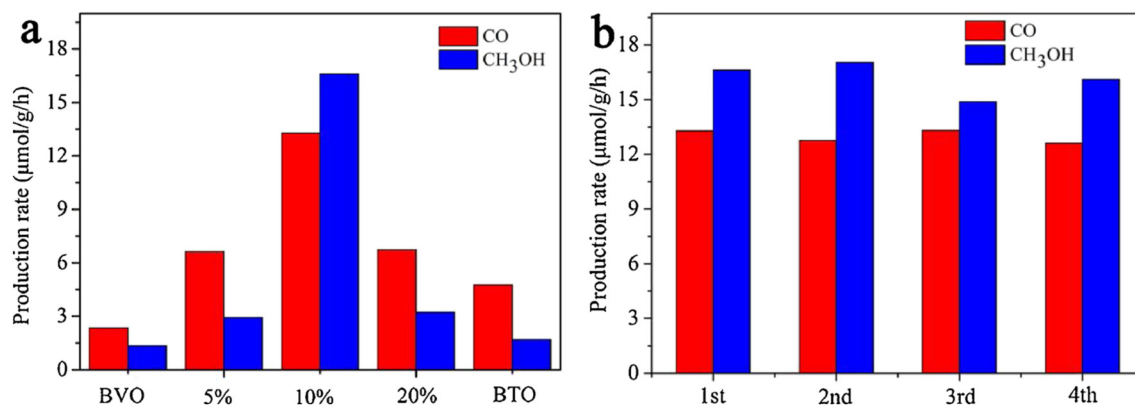


Fig. 8 (a) CH<sub>3</sub>OH and CO evolutions on BiVO<sub>4</sub>/Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> with different Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> contents and (b) photocatalytic activity stability of the BiVO<sub>4</sub>/10% Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> sample. Reprinted with permission from ref. 123. Copyright 2020, Elsevier.



coupled it with an Au cathode to achieve better conversion efficiency for CO<sub>2</sub>.<sup>126</sup> The Z-schematic pathway for charge carriers was constructed using SrTiO<sub>3</sub>:Rh and BiVO<sub>4</sub>.<sup>127</sup> In this work, a powder of the photocatalyst was used without adjusting the pH. It is worth noting here that the conversion of CO<sub>2</sub> to CO was progressed without any addition of additives.

### 3.3 Bi<sub>2</sub>WO<sub>6</sub>

Bi<sub>2</sub>WO<sub>6</sub>, belonging to an Aurivillius family of oxides, has been widely researched for its photocatalytic activity owing to its structure, composition and electronic property. Owing to the presence of [Bi<sub>2</sub>O<sub>2</sub>] and perovskite-type layers, Bi<sub>2</sub>WO<sub>6</sub> possesses a narrow band gap, which is around 2.6 eV. Due to sluggish reaction kinetics and the high rate of recombination of photoinduced charge carriers, the photocatalytic performance is poor.<sup>128</sup> Therefore, in order to improve the photocatalytic activity, several modifications have been made to Bi<sub>2</sub>WO<sub>6</sub> such as morphological control, heterojunction construction and doping.<sup>129</sup> It is important to have an update on the recent works on Bi<sub>2</sub>WO<sub>6</sub> to design any new material or to modify the existing photocatalyst. As the band gap of Bi<sub>2</sub>WO<sub>6</sub> is wider and unable to utilize the maximum visible light, heterojunctions have been constructed with other semiconductors such as Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub>, TiO<sub>2</sub>, Cu<sub>2</sub>O, InVO<sub>4</sub>, C<sub>3</sub>N<sub>4</sub>, BiOBr and BiOI.<sup>130–134</sup>

NiO, with a narrow band gap of ~2.5 eV, which can efficiently absorb visible light, was composited with Bi<sub>2</sub>WO<sub>6</sub>, which gave an S-scheme charge transfer. The heterojunction yielded CO and CH<sub>4</sub> with 46.9 and 12.1 μmol g<sup>-1</sup>, respectively, with the CO\* intermediate.<sup>135</sup> Lulu Zhao *et al.* attempted to improve the selectivity of the catalyst towards CO from CO<sub>2</sub> by substituting Bi<sup>3+</sup> and Ag<sup>+</sup> ions *via* the liquid-phase exchange process.<sup>136</sup> The incorporation of Ag<sup>+</sup> not only improved the adsorption of CO<sub>2</sub> and H<sub>2</sub>O but also enhanced the separation of the charge carriers.<sup>136</sup> Ultrathin Bi<sub>2</sub>WO<sub>6</sub> nanosheets with Ag<sup>+</sup> and Bi<sup>3+</sup> exhibited the

conversion of CO<sub>2</sub> to CO with a yield of 116 μmol g<sup>-1</sup> and with a selectivity of 95.7% after 6 h of the reaction without using any sacrificial agents. *In situ* DRIFT suggested that the intermediate formed was COOH\*, which is then converted to thermodynamically stable CO\*. It was possible to obtain methane *via* CO<sub>2</sub> photoreduction on Bi<sub>2</sub>WO<sub>6</sub> by modifying the surface with surface plasmon resonance. Precisely controlling the oxygen vacancy in Bi–O–Bi and W–O–W led to high selectivity towards CH<sub>4</sub>. The vacancy created an energy level that is very close to the conduction band, which helped in improving the life span of the charged carriers. To further improve the charge transport pathway, Bi<sub>2</sub>WO<sub>6</sub> was covalently heterostructured with Bi<sub>2</sub>O<sub>3</sub>. The Bi<sub>2</sub>O<sub>3</sub> nanosheets present on the Bi<sub>2</sub>WO<sub>6</sub> surface rendered more active sites, which enhanced the adsorption of CO<sub>2</sub> on the surface.

Graphdiyne (GDY) is explored as a potential material for solar energy harvesting since its first synthesis.<sup>137,138</sup> An ultrathin heterojunction of GDY and Bi<sub>2</sub>WO<sub>6</sub> was prepared by a simple hydrothermal method because GDY is an excellent material for efficient charge transfer.<sup>139</sup> Also, the increased surface area helped improve the CO<sub>2</sub> adsorption on the photocatalyst. GDY/Bi<sub>2</sub>WO<sub>6</sub> yielded 2.13 and 0.23 μmol h<sup>-1</sup> g<sup>-1</sup> of CH<sub>3</sub>OH and CH<sub>4</sub>, respectively. The reduction of CO<sub>2</sub> yielded CH<sub>3</sub>OH and CH<sub>4</sub> (Fig. 9).<sup>139</sup>

Further, to enhance the light absorption ability of the material, the hierarchical hollow structured heterojunction of Bi<sub>2</sub>WO<sub>6</sub>/TiO<sub>2</sub> was constructed by the *in situ* synthetic technique. This heterojunction interface generated the Bi<sup>(3-x)+</sup> active site, which could suppress the charge carrier recombination very effectively. In producing CO *via* CO<sub>2</sub> photoreduction, this heterojunction was better than that of pristine Bi<sub>2</sub>WO<sub>6</sub> and Bi<sub>2</sub>WO<sub>6</sub>/TiO<sub>2</sub>.<sup>27</sup> Similarly, Bi<sub>2</sub>WO<sub>6</sub> was heterojunctioned with other semiconductors such as InVO<sub>4</sub>, La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, and ZnV<sub>2</sub>O<sub>6</sub> either to improve the light absorption ability or to suppress the recombination rate of electron–hole pairs.<sup>140–142</sup>

Qiaoya Tang *et al.* constructed an S-scheme heterojunction of C<sub>3</sub>N<sub>4</sub>/Bi<sub>2</sub>WO<sub>6</sub> using the electrostatic self-assembly

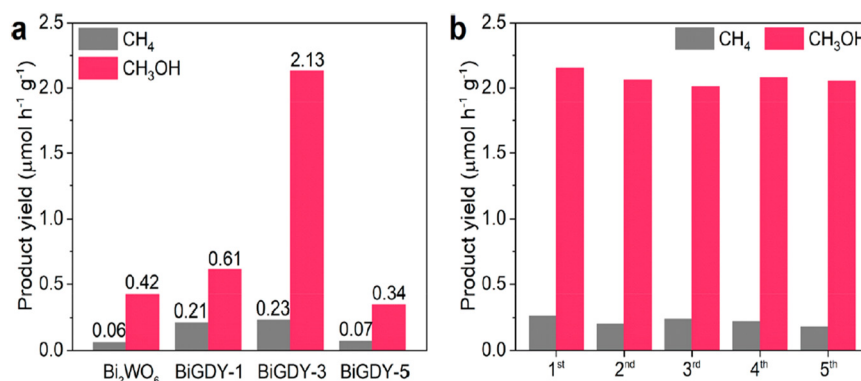
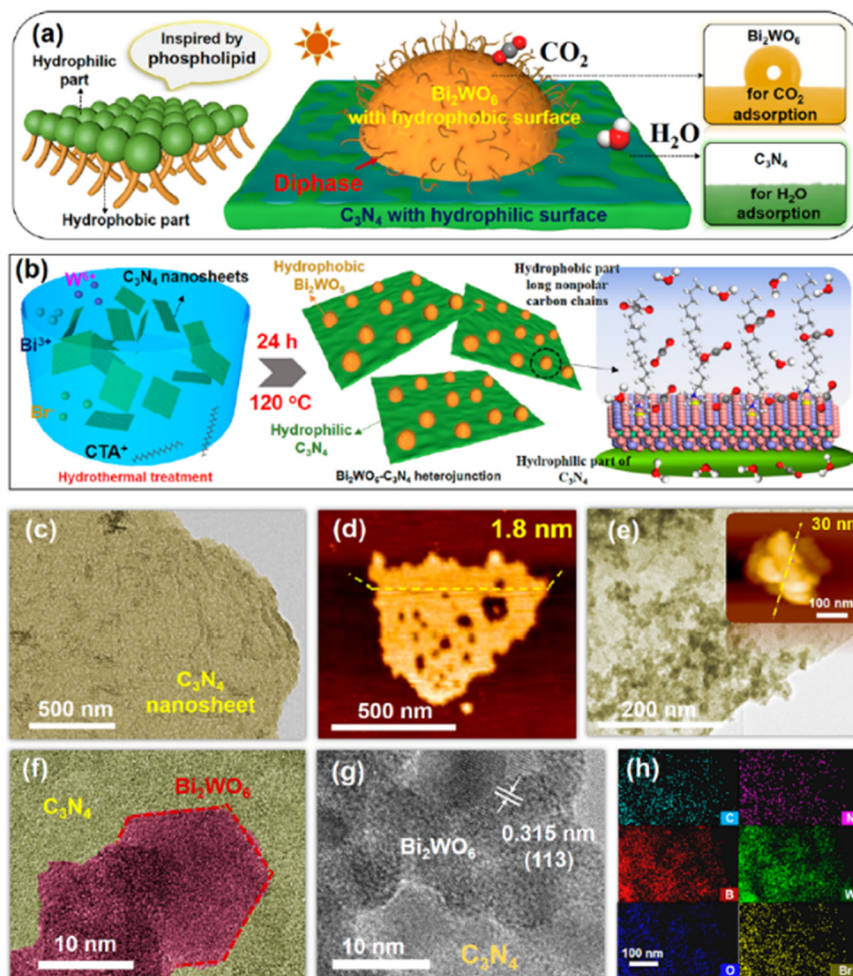


Fig. 9 (a) Photocatalytic CO<sub>2</sub> reduction performance of samples. (b) Cycling tests of the GDY/Bi<sub>2</sub>WO<sub>6</sub> heterojunction (BiGDY). Reproduced with permission from ref. 139. Copyright 2021, American Chemical Society.





**Fig. 10** (a) Schematic of the hydrophobic  $\text{Bi}_2\text{WO}_6$ -hydrophilic  $\text{C}_3\text{N}_4$  photocatalyst and the distribution of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . (b) Schematic of the preparation of a phospholipid-mimicking photocatalyst. (c) TEM image and (d) AFM image of  $\text{C}_3\text{N}_4$ . (e) TEM image and AFM image (inset) of  $\text{Bi}_2\text{WO}_6$ -CN. (f and g) HR-TEM images of  $\text{Bi}_2\text{WO}_6$ - $\text{C}_3\text{N}_4$ . (h) EDS elemental mapping of  $\text{Bi}_2\text{WO}_6$ - $\text{C}_3\text{N}_4$ . Reproduced with permission from ref. 144. Copyright 2024, American Chemical Society.

method.<sup>143</sup> The authors claimed that the formed ultrathin 2D/2D  $\text{C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$  heterostructure offers abundant reaction sites, which promote efficient charge transfer. Yunpeng Liu *et al.* introduced hydrophobic and hydrophilic ends in the diphasic photocatalyst to solve the competitive adsorption issue of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This amphipathic diphasic hydrophobic and hydrophilic photocatalyst not only inhibited the recombination of charge carriers but also could enrich  $\text{CO}_2$  and  $\text{H}_2\text{O}$  on hydrophobic and hydrophilic surfaces, respectively, as depicted in Fig. 10.<sup>144</sup>

In an effort to improve the yield of  $\text{CH}_4$  in  $\text{CO}_2$  photoreduction, Yan-Yang Li *et al.* modified  $\text{Bi}_2\text{WO}_6$  with chloride ions to study the influence of protons produced during the water oxidation on  $\text{CH}_4$  generation.<sup>145</sup> The density functional theory confirmed the mappings of  $\text{Bi}_2\text{WO}_6$ - $\text{C}_3\text{N}_4$ . The chloride ions present on the surface of  $\text{Bi}_2\text{WO}_6$  nanosheets not only promoted water oxidation but also favoured the formation of the  $\text{CHO}^*$  intermediate, which facilitated the formation of  $\text{CH}_4$ . Due to the presence

of chloride ions on the surface, the rate of the oxidation half-reaction goes smoothly, which indirectly promotes the reduction half-reaction ( $\text{CO}_2$  reduction).<sup>145</sup> As 2D/2D nanosheets provide a large specific surface area and rich active sites, Yong Jiang *et al.* fabricated the heterojunction of  $\text{CsPbBr}_3/\text{Bi}_2\text{WO}_6$ .<sup>146</sup> This enabled Z-scheme charge transfer and reduced charge carrier recombination to obtain the yields of  $1582.0 \mu\text{mol g}^{-1}$  for  $\text{CO}$  and  $8602 \mu\text{mol g}^{-1}$  of  $\text{CH}_4$ .<sup>146</sup>

Black phosphorous (BP) is a 2D material that is considered a potential candidate for photocatalytic applications because it provides a short diffusion length for the charge carriers. Because BP has a large specific area, it offers ample reaction sites for  $\text{CO}_2$  adsorption. Therefore, BP has been used for constructing heterojunctions with  $\text{Bi}_2\text{WO}_6$  because it is believed to accelerate the multistep electron process and dimerization of the C-C bond. Minghui Zhang *et al.* fabricated 2D/2D BP/ $\text{Bi}_2\text{WO}_6$  by the electrostatic assembly method.<sup>147</sup> Organic oxidation to value-added products was coupled with  $\text{CO}_2$  reduction, which lowered the



thermodynamic barrier for water oxidation. In this regard, benzylamine, which is a derivative of the renewable biomass, was used for organic oxidation to give imines as a high-value product. The adsorption study revealed that  $\text{Bi}_2\text{WO}_6$  with BP exhibited more active sites for  $\text{CO}_2$  adsorption. In addition to this, benzylamine provided alkaline media, which increased the solubility of  $\text{CO}_2$  in the solution. *In situ* Fourier transform infrared (FTIR) suggested that  $\text{CO}^*$  and  $\text{CH}_3^*$  were the intermediates for the conversion of  $\text{CO}_2$  to  $\text{C}_2\text{H}_5\text{OH}$ .<sup>136</sup> To harvest visible light absorption and to improve charge transfer, g- $\text{C}_3\text{N}_4$  was introduced on  $\text{Bi}_2\text{WO}_6$ . The photocatalytic performance was further enhanced by incorporating reduced graphene oxide (rGO).<sup>143,148</sup> In another report, ultrathin 2D/2D  $\text{Bi}_2\text{WO}_6/\text{g-C}_3\text{N}_4$  offered abundant contact interfaces with more accessible reaction sites that exhibited higher selectivity for CO generation compared to  $\text{CH}_4$ . The higher content of  $\text{Bi}_2\text{WO}_6$  hampered the performance of the composite, as it could shield the incident photons striking the catalyst surface and hinder the bandgap excitation process. Furthermore, the composite retained its performance even after four consecutive cycles.<sup>143</sup> These 2D/2D heterojunctions with face-to-face interfaces could lower the intrinsic resistance and boost the charge carrier separation process.<sup>149</sup>

The deposition of QDs like  $\text{Cs}_3\text{Bi}_2\text{Br}_9$  on the  $\text{Bi}_2\text{WO}_6$ -nanosheets could selectively promote the  $\text{CO}_2$  reduction reactions to form CO under visible light.<sup>134</sup> This unique 0D/2D (dot-to-face) geometry and lead-free bismuth halide perovskite semiconductor remained as an added advantage for this composite. The larger surface area of 2D sheets enabled the finer distribution of QDs on their surface, which not only resulted in a stable heterojunction but also lowered the distance for the charge carrier migration process. The preparation method was flexible as it only involved the dispersion of positively charged QDs on the negatively charged  $\text{Bi}_2\text{WO}_6$  sheets in isopropanol suspension through the electrostatic self-assembly approach. This strategy benefits from the prospect of retaining the pristine morphology of the concerned semiconductors during the heterojunction formation. The ESR analysis revealed the generation of both hydroxyl and superoxide radicals, which further confirmed the formation of the S-scheme heterojunction between them.<sup>134</sup>

### 3.4 $\text{Bi}_2\text{MoO}_6$

$\text{Bi}_2\text{MoO}_6$  is also found to be an interesting material that belongs to the Aurivillius oxide family. The structure of  $\text{Bi}_2\text{MoO}_6$  consists of alternating arrays of  $[\text{Bi}_2\text{O}_2]$  and  $[\text{MoO}_6]$  octahedral layers. This ternary metal oxide is an *n*-type semiconductor possessing a narrow band gap that can utilize visible light of the solar spectrum.<sup>150,151</sup> It is possible to effectively tune the electronic distribution and morphology to optimize the photocatalytic application towards  $\text{CO}_2$  reduction. By changing the temperature, reaction time and solvent, it is easier to modify the

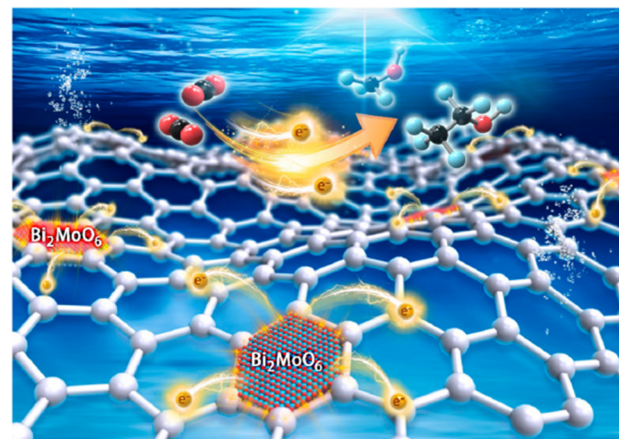
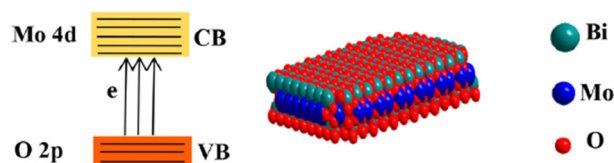


Fig. 11 Unit cell model of  $\text{Bi}_2\text{MoO}_6$  and electron transfer. Reproduced with permission. Reprinted with permission from ref. 152. Copyright 2020, American Chemical Society.

morphology of  $\text{Bi}_2\text{MoO}_6$ . Therefore, enormous efforts have been put into improving the photocatalytic performance of  $\text{Bi}_2\text{MoO}_6$  by morphological control and heterojunction compositing.

Dai *et al.* grew  $\text{Bi}_2\text{MoO}_6$  QDs on rGO scaffolds using an economically viable hydrothermal method.<sup>152</sup> Due to the high surface area of rGO, the dispersion of  $\text{Bi}_2\text{MoO}_6$  QDs was enhanced. The electron migration from  $\text{Bi}_2\text{MoO}_6$  QDs to rGO was facile because rGO exhibited excellent electrical conductivity. The photocatalytic mechanism is illustrated in Fig. 11.

Yu *et al.* fabricated a hierarchical heterostructure of 2D nanosheets of  $\text{Bi}_2\text{MoO}_6$  grown on 1D  $\text{In}_2\text{S}_3$  using the solvothermal technique. The hollow nanotubes of the  $\text{In}_2\text{S}_3$  nanostructure were designed using the MIL-68 precursor. The surface oxygen vacancy was created by using *N,N,N',N'*-tetramethylethylenediamine (TMEDA). However, the morphology of  $\text{Bi}_2\text{MoO}_6$  nanosheets was distorted to give a particle-like morphology when TMEDA was used to introduce surface oxygen vacancies.<sup>153</sup> The presence of the interfacial Mo-S bond in  $\text{Bi}_2\text{MoO}_6/\text{ZnIn}_2\text{S}_4$  boosted the production of CO from  $\text{CO}_2$  reduction reactions.<sup>151</sup> The *in situ* loading of  $\text{ZnIn}_2\text{S}_4$  nanoflakes on the porous microspheres of  $\text{Bi}_2\text{MoO}_6$  under the solvothermal conditions offered plentiful catalytic sites for  $\text{CO}_2$  adsorption and activation processes. Furthermore, the hierarchical structures enhanced the visible light absorption and possessed good photostability and reusability. The generation of superoxide and hydroxyl radicals, as confirmed from the ESR analysis, validated the formation of the S-scheme heterojunction between them.<sup>151</sup>



The oxygen-vacancy engineered  $\text{Bi}_2\text{MoO}_{6-x}/\text{MoS}_2$  was active for  $\text{CO}_2$  reduction to form  $\text{CO}$ , wherein oxygen vacancies were obtained from pristine  $\text{Bi}_2\text{MoO}_6$  via a simple annealing step. It is interesting to note that the oxygen vacancies did not disrupt the microsphere-like morphology of the host matrix, and the density of oxygen vacancies increased upon composite formation with  $\text{MoS}_2$ -nanosheets. The presence of these oxygen vacancies lowered the bandgap of the host matrix and acted as effective electron sink to delay the recombination of charge carriers and also reduced the work function of the host matrix, which indirectly decreased the energy required for the electron transfer process.<sup>154</sup>

Maryam Ahmadi *et al.* heterojunctioned  $\text{Bi}_2\text{MoO}_6$  with the benchmark photocatalyst  $\text{TiO}_2$  to reduce the rate of recombination of photogenerated electron-hole pairs.<sup>155</sup> The synergistic effect was achieved by compositing  $\text{Bi}_2\text{MoO}_6$  with  $\text{TiO}_2$ , as the band gap of both materials achieved a staggered configuration.  $\text{Bi}_2\text{MoO}_6$  nanosheets were decorated with  $\text{TiO}_2$  nanobelts by a simple solvothermal method. As cocatalysts acted as electron scavengers, Pt-Cu was decorated on the composite by the reduction method. It was noticed that the photoresponse of the photocatalyst increased, and  $34.6 \mu\text{mol g}^{-1}$  of methane was obtained for  $\text{Bi}_2\text{MoO}_6/\text{TiO}_2$ . Once the Pt-Cu were loaded on the composite, methane production was increased further as the cocatalyst helped trap the electrons and reduce the recombination rate.<sup>155</sup>

Other metal oxide semiconductor materials have also been heterojunctioned such as a spinel compound  $\text{ZnFe}_2\text{O}_4$ , which produced  $\text{CO}$  and  $\text{CH}_4$ .<sup>156</sup> The S-scheme pathway helped in a slight improvement of the  $\text{CO}_2$  reduction; the catalyst needs to be improved to achieve better photocatalytic performance. The 2D/2D  $\text{Bi}_2\text{MoO}_6/\text{Zn}_3\text{V}_2\text{O}_8$ , which formed an S-scheme, produced  $\text{CO}$  and  $\text{CH}_4$ .<sup>157</sup>

Nanosheets, belts, particles and spheres of  $\text{Bi}_2\text{MoO}_6$  have been synthesized, but reports on the QDs of  $\text{Bi}_2\text{MoO}_6$  are uncommon.<sup>158-160</sup> Weili Dai *et al.* anchored QDs of  $\text{Bi}_2\text{MoO}_6$  on 2D rGO sheets, which act as an electron reservoir, helping boost  $\text{CO}_2$  reduction. QDs  $\text{Bi}_2\text{MoO}_6/2\text{D}$  rGO produced  $84.8 \mu\text{mol g}^{-1}$  of methanol and  $57.5 \mu\text{mol g}^{-1}$  of ethanol, which are the highest among bismuth-based photocatalysts in the reduction of  $\text{CO}_2$ .<sup>152</sup> Further, the QDs of  $\text{Bi}_2\text{MoO}_6$  were deposited on pomelo-peel derived carbon (CPP) to improve the photocatalytic property of the catalyst. The CPP possesses a high specific surface area and has excellent thermal conductivity. As the photothermal temperature increases, it not only enhances the migration rate of the electrons and holes but also promotes the adsorption of  $\text{CO}_2$ . Mingnv Guo *et al.* synthesized 0D/3D CPP-A/ $\text{Bi}_2\text{MoO}_6$  to achieve a photothermal synergy to effectively utilize the solar spectrum.<sup>161</sup> As the temperature increases up to  $100^\circ\text{C}$ , the migration ability is increased, and a C-O-Bi bridge is formed, which enhances the electron transfer at the interface. This work provides a solution for the bottleneck

problem of poor charge carrier transport in photothermal catalytic activity.<sup>161</sup>

By combining both *n*-type semiconductors  $\text{In}_2\text{S}_3$  and  $\text{Bi}_2\text{MoO}_6$ , an S-scheme was achieved to design an efficient photocatalyst. 2D nanosheets of  $\text{Bi}_2\text{MoO}_6$  grown on 1D nanotubes of  $\text{In}_2\text{S}_3$  reduced the carrier diffusion length. The Z-scheme heterojunctions such as  $\text{Bi}_2\text{MoO}_6/\text{CdS}$  and  $\text{Bi}_2\text{MoO}_6/\text{CeO}_2$  have also been constructed to improve the charge carrier transport.<sup>162,163</sup> An S-scheme heterostructure can also be achieved from  $\text{ZnIn}_2\text{S}_4$  decorated on  $\text{Bi}_2\text{MoO}_6$ , where the Mo-S bond at the interface helps in improving the photocatalytic activity.<sup>151</sup> S-scheme heterostructures can also be achieved from chalcogenides, especially with MnS. Diethylenetriamine (DETA) ammonia treated MnS hollow sphere heterostructured with plasmonic Bi enhanced  $\text{CO}_2$  reduction rate of  $\text{Bi}_2\text{MoO}_6$ .<sup>164</sup> The presence of basic functional groups on DETA reduced the activation energy of acidic  $\text{CO}_2$ , whereas the surface plasmon effect from Bi produced hot electrons and decreased the recombination rate of charge carriers. This combined effect helped boost the  $\text{CO}_2$  photocatalytic reduction reaction.

Table 1 illustrates the different interfacial engineering of bismuth-based materials with various other compounds and their respective  $\text{CO}_2$  conversion products. The synthesis method and charge carrier pathway followed by the heterojunction are also mentioned. It is interesting to note that most of the bismuth-based materials are fabricated by wet chemical approaches such as hydrothermal and solvothermal methods. However, these techniques pose several challenges, as the materials' purity and morphology are sensitive to the synthesis temperature and reaction time. Therefore, the reproducibility of the structural-morphological features would be difficult for the large-scale synthesis.<sup>165,166</sup>

Other bismuth containing materials, such as  $\text{Bi}_{12}\text{O}_{17}\text{-Br}_2/\text{g-C}_3\text{N}_4$ ,  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2/\text{g-C}_3\text{N}_4$ ,  $\text{Bi}_3\text{NbO}_7/\text{g-C}_3\text{N}_4$ ,  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}/\text{Bi}_2\text{O}_3$ ,  $\text{Cs}_2\text{CuBr}_4/\text{Bi}_2\text{O}_3$ ,  $\text{BiOIO}_3/\text{CdS}$  and  $\text{Bi/Bi}_4\text{V}_2\text{O}_{11}$ , are explored for  $\text{CO}_2$  photocatalytic conversion.<sup>176-183</sup> In particular, the presence of interfacial Bi-N bonds and the nitrogen vacancy in  $\text{Bi}_{12}\text{O}_{17}\text{Br}_2/\text{g-C}_3\text{N}_4$  achieved simultaneous tetracycline degradation and  $\text{CO}_2$  reduction reactions.<sup>177</sup> In fact, the photocatalytic reduction of  $\text{CO}_2$  was improved in the presence of tetracycline compared to rhodamine B and phenol molecules, which was attributed to the superior electron-donating ability of TC. The flower-like  $\text{Bi}_{12}\text{O}_{17}\text{Br}_2$  were decorated on the defective  $\text{g-C}_3\text{N}_4$  surface via the wet chemical approach. The presence of defects was important to drive the coupled photocatalytic reactions. It was proposed that  $^*\text{CO}_2$  was transformed to  $^*\text{COOH}$  through a hydrogenation step, which upon further protonation yielded  $^*\text{CO}$ , which was feasible for the desorption from the composite surface. This work is a classical illustration of win-to-win strategy to achieve both environmental and energy related issues.<sup>177</sup> Alternatively,  $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2/\text{g-C}_3\text{N}_4$  promoted the formation of  $\text{CH}_4$  via two-



**Table 1** Comparison of heterojunctions of bismuth-based materials and their photocatalytic conversion of CO<sub>2</sub> along with synthesis technique

| Bismuth-based material                                              | Preparation method                                                                                | Nature of the heterojunction | Products: production rate in $\mu\text{mol g}^{-1} \text{h}^{-1}$ | Ref. |
|---------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|------------------------------|-------------------------------------------------------------------|------|
| BiOCl/BiOBr                                                         | Hydrothermal<br>Temperature – 160 °C<br>Time – 12 h                                               | Type-I                       | CO: 7.353                                                         | 84   |
| Bi <sub>2</sub> WO <sub>6</sub> /TiO <sub>2</sub>                   | Solvothermal                                                                                      | Type-II                      | CO: 43.7                                                          | 27   |
| BiOCl/Bi <sub>2</sub> WO <sub>6</sub>                               | Hydrothermal<br>Temperature – 120 °C<br>Time – 12 h                                               | Type-II                      | CO: 6.63                                                          | 76   |
| BiOBr/Bi <sub>2</sub> S <sub>3</sub>                                | Hydrothermal<br>Temperature – 180 °C<br>Time – 2 h                                                | Type-II                      | CO: 103 500                                                       | 92   |
| BiOBr/CoAl LDH                                                      | Hydrothermal<br>Temperature – 160 °C<br>Time – 12 h                                               | Type-II                      | CO: 4.096<br>CH <sub>4</sub> : 4.174                              | 96   |
| BiOI/In <sub>2</sub> O <sub>3</sub>                                 | Hydrothermal method<br>Temperature – 180 °C<br>Time – 12 h                                        | Type-II                      | CO: 11.98<br>CH <sub>4</sub> : 5.69                               | 107  |
| BiVO <sub>4</sub> /Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>  | Hydrothermal<br>Temperature – 160 °C<br>Time – 21 h                                               | Type-II                      | CH <sub>3</sub> OH: 16.6<br>CO: 13.29                             | 123  |
| BiVO <sub>4</sub> /Bi <sub>2</sub> S <sub>3</sub> /MnO <sub>3</sub> | Selective epitaxial growth<br>Temperature – 180 °C<br>Time – 90 min                               | Z-scheme                     | CH <sub>3</sub> OH: 20 ± 2.33                                     | 60   |
| BiOBr/HNb <sub>3</sub> O <sub>8</sub>                               | Self-assembly ultrasonic dispersion for 30 min                                                    | Z-scheme                     | CO: 164.6                                                         | 167  |
| g-C <sub>3</sub> N <sub>4</sub> /BiOI/RGO                           | Hydrothermal method<br>Temperature – 160 °C<br>Time – 6 h                                         | Z-scheme                     | CO: 21.85                                                         | 168  |
| Co-MOF/Bi <sub>2</sub> MoO <sub>6</sub>                             | Solvothermal, followed by the <i>in situ</i> growth method<br>Temperature – 165 °C<br>Time – 16 h | Z-scheme                     | CO: 19.76<br>CH <sub>4</sub> : 8.24                               | 169  |
| BiVO <sub>4</sub> /Cu <sub>2</sub> O/Bi                             | Solvothermal<br>Temperature – 120 °C<br>Time – 6 h                                                | Z-scheme                     | CH <sub>4</sub> : 1.8<br>CO: 8.4                                  | 170  |
| In <sub>2</sub> O <sub>3</sub> /Bi <sub>2</sub> S <sub>3</sub>      | Hydrothermal, followed by ultrasonication<br>Temperature – 180 °C<br>Time – 24 h                  | Z-scheme                     | CO: 2.67                                                          | 171  |
| Quinacridone/BiVO <sub>4</sub>                                      | Self-assembly method<br>Stirring for 1 h                                                          | Z-scheme                     | CO: 407<br>CH <sub>4</sub> : 29                                   | 172  |
| BiOCl/C <sub>3</sub> N <sub>4</sub>                                 | Hydrothermal<br>Temperature – 120 °C<br>Time – 12 h                                               | Z-scheme                     | CO: 45.33                                                         | 173  |
| BiOBr-(001)/Bi <sub>2</sub> SiO <sub>5</sub> /Bi                    | Solvothermal method<br>Temperature – 190 °C<br>Time – 12 h                                        | S-scheme                     | CO: 234.05                                                        | 74   |
| BiOBr/Bi <sub>2</sub> WO <sub>6</sub>                               | Hydrothermal<br>Temperature – 160 °C<br>Time – 6 h                                                | S-scheme                     | CO: 55.17                                                         | 94   |
| BiOBr/Cu <sub>2</sub> O                                             | Hydrothermal<br>Temperature – 160 °C<br>Time – 12 h                                               | S-scheme                     | CH <sub>4</sub> : 22.78                                           | 97   |
| BiOBr/CsPbBr <sub>3</sub>                                           | Self-assembly process<br>Overnight magnetic stirring in the dark                                  | S-scheme                     | CO: 104.4<br>CH <sub>4</sub> : 10.0                               | 103  |
| BiVO <sub>4</sub> /CsPbBr <sub>3</sub>                              | <i>In situ</i> colloidal growth method                                                            | S-scheme                     | CO: 103.5                                                         | 122  |
| Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> /porous BiOCl       | Dipping method<br>Magnetic stirring for 1 h                                                       | S-scheme                     | CO: 25.5                                                          | 174  |
| BiVO <sub>4</sub> /Cu–Bi                                            | Solvothermal<br>Temperature – 120 °C<br>Time – 6 h                                                | Oxygen vacancy               | CO: 2.96                                                          | 56   |
| BiOCl/Br–O <sub>v</sub>                                             | Solvothermal<br>Temperature – 160 °C<br>Time – 10 h                                               | Defects                      | CO: 7.37                                                          | 175  |

Note: readers are requested to follow the respective references for more information.

electron and two-proton reaction pathways.<sup>181</sup> On the contrary, Bi<sub>3</sub>NbO<sub>7</sub>/g-C<sub>3</sub>N<sub>4</sub> promoted the formation of CH<sub>4</sub>

as the reduction pathway proceeded through the formation of CH<sub>3</sub>O\* and CHO\* fragments.<sup>178</sup> Lee *et al.* reported that



CdS-nanorods/BiOIO<sub>3</sub>-nanosheets (1D/2D) selectively generated CO and minor amounts of H<sub>2</sub> during the CO<sub>2</sub> reduction reactions, and the activity was retained even after four consecutive cycles.<sup>182</sup> The line interfacial contact between the integrated materials promoted the charge carrier lifetime with minimal recombination pathways.<sup>184</sup> A significant improvement in photocatalytic performance was noticed, yet these materials must be explored further to enhance the conversion of CO<sub>2</sub> to value-added products.

## Conclusions and perspectives

The photocatalytic reduction of CO<sub>2</sub> into fuels and simple chemicals is a versatile approach that can simultaneously address environmental issues, carbon neutrality and energy demands. The high degree of chemical inertness of CO<sub>2</sub>, sluggish dynamics of multi-electron reduction reactions and massive charge carrier recombination in single-phase photocatalytic active materials have driven the emergence of heterojunction photocatalysts. In this context, bismuth-based materials are found to be an interesting class of materials because they possess a narrow band gap and a favourable electronic structure for the photocatalytic CO<sub>2</sub> reduction reaction. Although notable progress has been achieved with Bi-based heterojunctions, the achieved efficiency is still far from satisfactory, as the presence of a single electric field may not always boost the charge carrier separation process. Thus, future research must essentially focus on the coupling of multiple electric fields, which will not only extend the carrier lifetime, but also allow their diffusion to react with the adsorbed species. Furthermore, designing and fabricating the hierarchical Bi-based heterojunctions comprising QDs, 1D, 2D and 3D forms would be even more advantageous from the perspective of improving the light harvesting capacity, surface reactions and charge carrier separation kinetics. In addition, some importance should be given to the preparation of NIR-responsive Bi-based materials, which would spotlight our interest in harvesting the complete solar spectrum for the photocatalytic reactions. From the viewpoint of charge carrier dynamics, steering the migration of charge carriers in a specific path without compromising their lifetimes requires a suitable interface during the fabrication of heterojunctions. Alongside, the coupling of the CO<sub>2</sub> reduction reaction with pollutant degradation, H<sub>2</sub>O<sub>2</sub> generation and the synthesis of organic compounds will fulfil our dream of achieving a win-win strategy comprising energy and environmental aspects.

This review summarizes the interfacial engineering carried out for bismuth-based materials in recent years for CO<sub>2</sub> reduction. A large number of reported works have demonstrated that interfacial engineering helps effectively enhance the charge separation, light absorption and adsorption of CO<sub>2</sub> on the surface of the photocatalyst. However, the conversion efficiency is far from the efficiency

required to implement in practical applications. Most of the interfacially engineered bismuth-based photocatalysts exhibit a rate of reduction of CO<sub>2</sub> less than 100 μmol g<sup>-1</sup>. It is also noticed from the previous literature that the product obtained from the photocatalytic reduction reaction is carbon monoxide. Though bismuth based materials show promising results in photoelectrochemical water splitting, the photocatalytic activity towards CO<sub>2</sub> reduction is insignificant even after interfacial engineering with several other competent materials. Therefore, attention must be paid to enhance the photocatalytic activity of bismuth-based materials to meet the practical requirements for photocatalytic CO<sub>2</sub> reduction.

## Conflicts of interest

Authors declare that there is no competing financial interest.

## Data availability

No data were used in this article.

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