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A review of nanostructured non-titania photocatalysts and hole scavenging agents for CO₂ photoreduction processes

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The imperative for the development of sustainable energy technologies to alleviate the heavy reliance on fossil fuels as well as to mitigate the serious environmental issues associated with CO₂ emission has fostered the development of solar fuels through CO₂ photoreduction. The well-documented TiO₂ and modified TiO₂-based photocatalysts have been shown to photoreduce CO₂ into hydrocarbons. Meanwhile, there is also an increasing interest in the utilisation of non-titania based materials, namely metal sulphides, oxides, oxynitrides and nitrides, for CO₂ photoreduction. Distinct from other published reviews, we discuss here recent progress made in designing metal sulphide, oxide, oxynitride and nitride photocatalysts for CO₂ photoreduction through morphological changes, aiming at providing a systematic summary of non-titania based materials for CO₂ photoreduction. Furthermore, the introduction of hole scavengers in order to maximise the CO₂ photoreduction efficiency is also reviewed.

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1. Introduction

Fossil fuels are currently unrivalled for energy generation, and our existing infrastructure is built to handle fossil fuels for transportation, heating and electricity.¹ Our heavy reliance on fossil fuels results in annual emissions of 32 Gt of CO₂.² This is likely to increase to 36–43 Gt by 2035, subject to policies governing CO₂ emissions and energy use, even with increasing renewable energy sources.³ To mitigate these environmental issues as well as alleviate our dependence on fossil fuels, harvesting the seemingly infinite solar energy and storing it in the form of chemical fuels hold significant promise to address current and future energy demands. Moreover, the chemical industry and a vast amount of chemical products rely heavily on using fossil fuel feedstock. This further motivates the development of sustainable processes to generate fuels and chemical feedstock from water and CO₂ using solar energy. Such a process is akin to photosynthesis in nature, and therefore, it is referred to as the artificial photosynthesis.

Photoelectrocatalytic reduction of CO₂ in aqueous suspensions using semiconducting powders was first proposed by Inoue *et al.* in 1979.⁴ Later in 1987, the photocatalytic reduction of CO₂ to CH₄ in the presence of H₂O was proposed by Thampi *et al.*⁵ Since then, an increasing number of studies on the photo(electro)catalytic reduction of CO₂ have been conducted (Fig. 1). Among these studies, almost 50% focused on the materials employed as photocatalysts for conversion of CO₂ under UV and/or visible irradiation. The rest of the studies

concentrated mainly on modelling or process development. The use of TiO₂ as a photocatalyst for CO₂ reduction has been extensively studied and has been reviewed elsewhere.^{6–10} However, the lack of systematic studies of non-TiO₂ semiconducting materials, namely metal sulphides, oxides, oxynitrides and nitrides, for CO₂ photoreduction (CO₂PR) has inhibited the development of these photocatalysts compared to titania-based photocatalysts.

Although different photocatalysts (*i.e.*, titania and non-titania based semiconductors) have been proposed in the literature, the overall CO₂PR conversion remains low especially under sunlight irradiation, making the CO₂PR system not practical for commercialisation. To further increase the efficiency of CO₂PR, the introduction of scavenging agents into the CO₂PR system has been proposed. However, so far, the introduction of hole scavenging agents has not been systematically studied, though studies started in the last century. Therefore, the necessity to systematically scrutinise the recent development of non-TiO₂ photocatalysts and hole scavenging agents for CO₂PR is of great demand.

There are enormous scientific and technical challenges involved in making even the simplest fuel, H₂, and even more so for carbon-based fuels by means of CO₂ photoreduction. Similar to other photocatalytic processes, solar-driven photocatalytic conversion of CO₂ in the presence of H₂O to hydrocarbon fuels uses semiconducting materials to harvest solar energy and provides active sites to allow the photocatalytic conversion process to occur. The basic steps of the photocatalytic process can be summarised as follows:

(1) generation of charge carriers (electron–hole pairs) by semiconducting materials upon absorption of photons with appropriate energy from the irradiation of light,

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(2) separation of charge carriers and their transportation to the surface of the photocatalyst, and

(3) chemical redox reactions between the charge carriers and the reactants.

CO₂PR with H₂O into fuels is illustrated in Fig. 2. TiO₂ was the first material used for CO₂PR,⁵ and since then it has been widely used because of its abundance, availability, high chemical stability, low cost and non-toxicity.¹² Despite the great effort made in the CO₂PR using TiO₂ and its derivative materials, the efficiency of the process remains low,⁷ mainly attributed to the following factors:

(a) Rapid recombination of photogenerated electron-hole pairs;¹⁰

(b) Mild reducing power;

• The potential of the conduction band electrons is only slightly more negative than the multi-electron reduction potentials of CO₂, thus providing a very small driving force, whereas the potential of the valence band holes is much more positive than the water oxidation potential.⁷

(c) Limited visible light absorption due to the wide bandgap (3.0–3.2 eV) of TiO₂.^{13,14}

Strategies including doping,^{15,16} coupling with semiconductors,^{17–19} dye sensitizing,^{20,21} surface modification^{22,23} etc. have been extensively used to improve TiO₂ photocatalysts and are summarised elsewhere.^{9,14,24,25} However, the two most commonly used methods for extending the absorption range to visible light, namely sensitization or doping, do not fully address the optical issue of wide bandgap materials. Sensitizing agents (e.g., dyes or quantum dots) often degrade when exposed to UV light and photogenerate oxidizing holes in TiO₂.⁷ Dopant atoms, on the other hand, can become the centers of charge recombination. Moreover, the additional energy states associated with foreign atoms are highly localized, resulting in suppressed charge mobility.²⁷ Hence, while TiO₂ remains a benchmark photocatalyst, there is a lot of interest in developing other materials for CO₂PR, such as carbon-based semiconductors (e.g., graphene-based composites,^{28,29} carbon nanotube composites,³⁰ g-C₃N₄ based composites^{31–33} and

hybrid organic–inorganic materials^{34–37}) and other inorganic transition or main group metal oxides, sulphides, oxynitrides, and nitrides. Since the use of carbon-based semiconductors for CO₂PR has been reviewed elsewhere,^{30,34,38,39} these photocatalysts are not be discussed herein.

Inorganic semiconductors, namely metal oxides, sulphides, oxynitrides and nitrides, are among the first semiconductors



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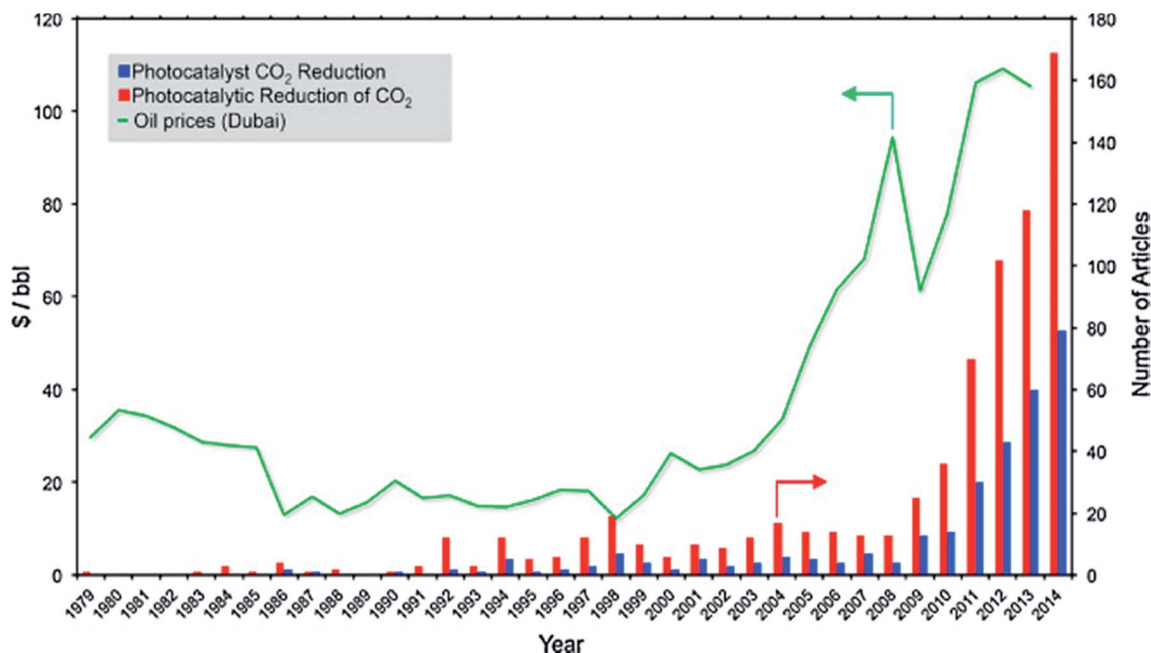


Fig. 1 Timeline for the number of articles published on CO₂ photoreduction vs. the price of oil. Reproduced from ref. 11 with permission.

used for solar-driven reactions. They possess relatively high stability, are low cost and absorb light consisting of photons with energy equal to or greater than their bandgap.⁴⁰ This very diverse group of materials includes both narrow and wide bandgap semiconductors; yet many of them offer a more favourable bandgap than TiO₂. Moreover, many recent CO₂PR developments follow similar trends to those for photocatalytic water splitting, as both processes share similar constraints on energy bands.^{41–43} Specifically, the quest for new semiconductor materials is focused on the following points:²⁷

- rising the valence band energy to decrease the bandgap,
- moving the conduction band to more reductive potentials,
- improving the quantum efficiency of exciton formation whilst suppressing charge recombination and

(d) using novel nanoscale morphologies to provide a large surface area with multiple photocatalytically active sites.

To achieve the quest mentioned above, different methods have been proposed previously and are reviewed in the following sections.

2. Non-TiO₂ materials for CO₂ photoreduction reactions

Although the position of conduction and valence bands is important for photocatalytic properties, the morphology of materials plays a critical role. Furthermore, manipulating the microstructure has also shown to alter the bandgap energy,⁴⁴ suppress the charge recombination,⁴⁵ enhance the diffusion of electrons towards the surface of photocatalysts,⁴⁶ induce quantum confinement effects⁴⁷ and provide more photocatalytic active sites, thereby enhancing the photocatalytic performance. In this section, nanostructured non-TiO₂ semiconducting materials for CO₂PR published in the last two decades are reviewed, including metal sulphides, oxides, oxynitrides and nitrides.

2.1 Sulphides

Sulphide semiconductors received a lot of attention for CO₂PR. This was because their valence band, made of 3p orbitals of the sulphur atoms, is located higher than those of their oxide analogues, resulting in the conduction band being more reductive.⁴² Many sulphides have a narrow bandgap (*e.g.*, PbS and Bi₂S₃), with the absorption onset in the visible and infrared regions. Amongst sulphide semiconductors, ZnS and CdS were the most studied sulphides for CO₂PR. ZnS is a wide bandgap semiconductor ($E_g = 3.66$ eV in the bulk); however, it possesses

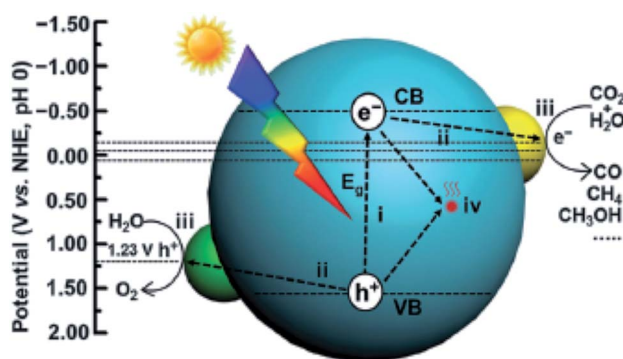


Fig. 2 Schematic illustration of photocatalytic CO₂ reduction with H₂O over a heterogeneous photocatalyst. The dotted lines indicate the thermodynamic potentials for water oxidation and CO₂ reduction into CO, CH₃OH and CH₄. Reproduced from ref. 26 with permission.



a strong reducing power of the conduction band ($E_{CB} = -1.85$ V vs. the NHE at pH 7).⁴⁸

Zinc-based materials. The surface area of the photocatalyst is one of the key factors that can significantly affect the efficiency of the photocatalytic process. Kočí *et al.* proposed the immobilization of ZnS on montmorillonite, a representative natural clay mineral, which possesses a high surface area and layered structure, to optimise the efficiency of the CO₂PR (Table 1 entry 1).⁴⁹ The study demonstrated that the amount of ZnS loaded affected the degree of agglomeration that consequently influenced the electronic configuration as well as the efficiency of the ZnS/montmorillonite nanocomposite in the CO₂PR under UV irradiation (254 nm). A similar approach was demonstrated by Petra *et al.*, in which ZnS was loaded onto large-surface-area SiO₂ (340 m² g⁻¹) to reduce CO₂ to formate using 2,5-dihydrofuran as the reducing agent.⁵⁰ The study revealed that the loading amount of ZnS significantly affected the yield and the optimal loading was 13% of ZnS into SiO₂, resulting in 7 mmol g⁻¹ h⁻¹ of HCOOH. Nonetheless, the fabricated samples with coverages above 7% of ZnS on the SiO₂ matrix could suppress the photo-corrosion of ZnS to Zn(0), which is the major disadvantage of sulphides in an aqueous dispersion because the oxidation of lattice S²⁻ ions leads to elemental sulphur and eventually to sulphate.⁵¹

Meng *et al.* proposed the co-doping of Cd and Cu into ZnS as one of the most active and optimised design routes for metal sulphide photocatalysts so far.⁵² It was found that the doping of Cu could promote the formation of S vacancies and narrow the bandgap energy of ZnS, whereas surface modification of Cu-doped ZnS with Cd²⁺ enhanced the product selectivity towards HCOOH (99%) under solar light irradiation. Recently, solid solutions of ZnLn₂S₄ with a flower-like microstructure decorated with a cubic CeO₂ co-catalyst have been shown to exhibit enhanced CH₃OH production (0.542 μmol g_{catalyst}⁻¹ h⁻¹) when compared to pristine CeO₂ and ZnLn₂S₄ (0.139 and 0.073 μmol g_{catalyst}⁻¹ h⁻¹, respectively) under visible light irradiation ($\lambda \geq 420$ nm).⁵³

Cadmium-based materials. CdS (2.4 eV and the absorption onset at 520 nm) is a narrow bandgap metal sulphide photocatalyst. Hence, CdS suffers from rapid recombination of photogenerated electron-hole pairs. In order to enhance the separation of photogenerated electron-hole pairs, surface-phase junctions deduced by the same semiconductors were proposed. Chai *et al.* fabricated a mixed-phase CdS that is composed of wurtzite and zinc-blende crystalline phases recently (Table 1 entry 2).⁵⁴ The fabricated sample exhibited a long photogenerated electron lifetime and efficient charge transfer. The maximum CO and CH₄ evolution rate was 1.61 and 0.31 μmol h⁻¹ g⁻¹, respectively, and these production rates were maintained even after 100 h.

The conduction band of CdS is less reductive ($E_{CB} = -0.9$ V at pH 7 vs. NHE) than that of ZnS. Therefore, CdS is always decorated with noble metals, such as Ag. For instance, Zhu *et al.* proposed that the loaded Ag could act as an electron trap as well as an active site for CO₂PR on CdS.⁵⁵ The photoproduction of CO was improved by three times when compared with that obtained with bare CdS. Alternatively, CdS can be supported with other

wide bandgap semiconductors to enhance its reducing power for CO₂PR. Kisch *et al.* found that the coupling of CdS with ZnS strongly enhanced the CO₂PR activity when compared to SiO₂-supported CdS or ZnS samples because CdS and ZnS can absorb light at ≤ 530 nm and ≤ 330 nm, respectively.⁵⁶ The study reported that 5 wt% CdS loaded onto ZnS induced a 40-fold and 16-fold enhancement in the production of HCOOH (~ 80 mM, $\lambda \geq 320$ nm, 3 h) when compared to unmodified CdS and ZnS, respectively. This strong enhancement was attributed to the electronic semiconductor-support interaction effect that improved the charge separation efficiency of the coupled semiconductor system. A similar observation was also reported by Kočí *et al.* recently, in which core-shell CdS/ZnS nanoparticles deposited on montmorillonite prepared by a one-pot synthesis exhibited enhanced CO₂PR activity in water under UV irradiation ($\lambda = 365$ nm).⁵⁷ The increase in the yield was due to the enhanced charge separation of CdS cores by ZnS shells, the increase of surface area and the inhibition of CdS photo-corrosion. CO₂PR performed with CdS coupled with Bi₂S₃, having smaller bandgap energy than CdS, was also reported.⁵⁹ The Bi₂S₃/CdS nanocomposite fabricated with 15 wt% Bi₂S₃ exhibited the highest methanol production from CO₂ (6.13 mmol g⁻¹ h⁻¹, Table 1 entry 3), which was at least 50% higher than those obtained with bare Bi₂S₃ (3.14 mmol g⁻¹ h⁻¹) and CdS (2.01 mmol g⁻¹ h⁻¹), under visible light irradiation. The enhanced photocatalytic activity suggested that the establishment of a heterojunction between CdS and Bi₂S₃ could improve charge separation and subsequently prolong the lifetime of photogenerated electron-hole pairs. Moreover, the surface area of the Bi₂S₃/CdS nanocomposite, which was 24–27 m² g⁻¹, was slightly higher than those of the bare CdS and Bi₂S₃ (12 and 21 m² g⁻¹, respectively). Hence, the synergistic effect of surface area and the heterojunction established between these two semiconductors had significantly improved the overall performance in CO₂PR. Increasing the specific surface area does not only provide more active sites for the photocatalytic reaction, but also affects the optical properties of the material. For instance, Jin *et al.* recently proposed that by increasing the length-to-width ratio of Bi₂S₃ nanoribbons, which increased the bandgap energy of Bi₂S₃ from 1.22 to 1.38 eV, the CH₃OH yield obtained was increased from 25.94 to 32.02 μmol g_{catalyst}⁻¹ h⁻¹ under visible light irradiation ($\lambda \geq 420$ nm).⁶¹ However, the coupling of Bi₂S₃ nanoribbons with CdS was not demonstrated. Hence, it will be interesting to see the performance of Bi₂S₃ nanoribbons/CdS nanocomposites in the CO₂PR.

The coupling of CdS with other metal oxides, such as WO₃, has been demonstrated recently. For instance, Jin *et al.* proposed the coupling of WO₃ hollow spheres with CdS to form a hierarchical Z-scheme to increase the CO₂PR efficiency.⁶² The coupling of WO₃-CdS had greatly enhanced the photo-conversion of CO₂ to CH₄ to ~ 1.0 μmol g_{catalyst}⁻¹ h⁻¹ under visible irradiation ($\lambda \geq 420$ nm), whereas pristine WO₃ and CdS only produced trace amounts of CH₄.

Recently, the synthesis of Zn_xCd_{1-x}S solid solutions has attracted extensive attention due to their versatility in tuning the band structures.^{63–65} Moreover, the introduction of Zn can



Table 1 Photocatalytic CO₂ reduction yields obtained with various photocatalysts

No.	Photocatalyst	Product(s) of CO ₂ photoreduction ($\mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$)	Light source	Ref.
Sulphides				
1.	ZnS/montmorillonite nanocomposite	CH ₄ 1.17 CO 0.125	UV 8 W Hg lamp ($\lambda = 254 \text{ nm}$)	49
2.	CdS wurtzite/zinc-blende nanohybrid	CO 1.61 CH ₄ 0.31	300 W Xe lamp ($\lambda \geq 420 \text{ nm}$)	54
3.	Bi ₂ S ₃ /CdS CdS wurtzite/zinc-blende nanohybrid	CH ₃ OH 6.13 $\text{mmol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ CO 1.61 CH ₄ 0.31	500 W Xe lamp ($\lambda \geq 320 \text{ nm}$) 300 W Xe lamp ($\lambda \geq 420 \text{ nm}$)	59 54
4.	Zn _x Cd _{1-x} S solid solution and tetra(4-carboxyphenyl)porphyrin iron(III) chloride	CO 1.28 μmol	300 W Xe lamp ($420 \text{ nm} < \lambda < 780 \text{ nm}$)	58
5.	Cu ₂ S/CuS	CH ₄ $46.21 \pm 6.50 \mu\text{mol m}^{-2} \text{h}^{-1}$	A.M 1.5 simulated sunlight	60
6.	RuO ₂ -modified Cu _x Ag _y In _z Zn _k S _m solid solutions	CH ₃ OH 118.5	1000 W Xe lamp ($\lambda > 400 \text{ nm}$)	69
Oxides				
7.	ZnO	CH ₃ OH 325	355 nm laser beam	74
8.	NiO	CH ₃ OH 388		
9.	Fluffy mesoporous ZnO	CO 0.73	8 W fluorescent tube (7 mW cm^{-2})	75
10.	N-doped ZnO	CO 0.04		
11.	ZnO plates	CO 763.5 ppm $\text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ CH ₄ 205.2 ppm $\text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$	300 W Xe arc lamp	76
12.	Ultralong and ultrathin single crystal Zn ₂ GeO ₄ nanoribbons	CH ₄ 25	300 W Xe arc lamp	77
13.	Zn ₂ GeO ₄ nanorods	CO 179 ppm $\text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ CH ₄ 35 ppm $\text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$	300 W Xe arc lamp	78
14.	RuO ₂ and Pt co-loaded Zn _{1.7} GeN _{1.8} O nano-sheaves	~55	300 W Xe arc lamp ($\lambda > 420 \text{ nm}$)	79
15.	ZnGa ₂ O nanosheet-scaffolded microspheres	69	300 W Xe arc lamp with an IR cut filter	80
16.	Zn ₂ SnO ₄ hexagonal nanoplates	47	300 W Xe arc lamp	81
17.	Ce-doped ZnFe ₂ O ₄	CO ~20	Visible light	82
18.	Quasi-cubic WO ₃	~0.34	300 W Xe lamp	83
19.	Ultrathin single crystal WO ₃	~1.1	300 W Xe arc lamp	84
20.	Ultrathin W ₁₈ O ₄₉	CH ₄ 2200	Full-arc Xe lamp	85
21.	Bi ₂ WO ₆ nanosheets with well-defined {001} facets	1.1	300 W Xe arc lamp	86
22.	BiWO ₆	CH ₃ OH 32.6	300 W Xe lamp ($\lambda > 420 \text{ nm}$)	87
23.	NaNbO ₃ nanowires	CH ₄ 653 ppm $\text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$	300 W Xe lamp	88
24.	KNb ₃ O ₈ nanobelts	CO 3.58	350 W Xe lamp	89
25.	HNb ₃ O ₈ nanobelts	CO 1.71		
26.	SrNb ₂ O ₆ nanorods	CO 51.2	400 W Hg lamp	90
27.	3% NiO _x -Ta ₂ O ₅ -1% immobilised on reduced graphene	CH ₃ OH 197.92	400 W metal halide lamp	91
28.	Core-shell Ni/NiO-loaded N-InTaO ₄	CH ₃ OH 160	Xe lamp (100 mW, $390 \leq \lambda \leq 770$)	92
29.	LaTa ₇ O ₁₉	CO 50	400 W Hg lamp	93
30.	CaTa ₄ O ₁₁	CO 70		
31.	1.0 wt% Ag-modified Ba-doped NaTaO ₃	CO ~50	400 W Hg lamp	94
32.	K ₂ YTa ₅ O ₁₅	CO 91.9	4000 W Hg lamp	95
33.	Ag-modified Ga ₂ O ₃	CO 10.5	UV light	96
34.	Lamellar BiVO ₄	CH ₃ OH 5.52	300 W Xe lamp (full spectrum)	97
35.	CuGa _{1-x} Fe _x O	CO ~9.2	300 W Xe arc lamp	98
36.	CoAl-layered double hydroxides	CH ₄ 4.2	500 W Xe lamp	99
Oxynitrides				
37.	Porous TaON	CH ₃ CHO 0.52 C ₂ H ₅ OH 2.03	300 W Xe lamp	100
38.	ZnAl ₂ O ₄ -modified ZnGa ₂ ON	CH ₄ 9.2	300 W Xe lamp ($\lambda \geq 420 \text{ nm}$)	101
Nitrides				
39.	GaN	CO 1130 CH ₄ 1.3	300 W Xe lamp	102
40.	Rh/Cr ₂ O ₃ -decorated GaN nanowires	CO 120 CH ₄ 3.5		



manipulate the structure of the surface atoms in CdS, which influences the adsorption or desorption of the reactants, intermediates and products in photocatalytic reactions.⁵⁸ In a very recent study, Li *et al.* integrated the well-defined floccule-like $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ solid solution (Fig. 3) with tetra(4-carboxyphenyl)porphyrin iron(III) chloride for CO_2 photoreduction under visible light irradiation.⁵⁸ The optimised photocatalyst, which was synthesized with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ at 0.25 : 0.75 (ZCS-1, Fig. 3), produced 1.28 μmol of CO with a selectivity of 93% after 4 h. However, pristine CdS and other synthesized $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ solid solutions produced less than 0.4 μmol of CO under visible light irradiation. The superior performance of ZCS-1 was attributed to the presence of sulphur vacancies that trapped photogenerated electrons, provided CO_2 adsorption sites and facilitated the interaction between the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ solid solution and tetra(4-carboxyphenyl)porphyrin iron(III) chloride, resulting in efficient interfacial electron transfer for the subsequent photocatalytic reduction reaction.

Copper-based materials. Cu_{2-x}S , which have been shown to exhibit localised surface resonance in the near infrared region, and CuS, which has a direct bandgap of 2.0 eV, are nearly ideal for optimal sunlight absorption.^{66,67} By carefully controlling the anodization voltage and temperature during the electrochemical anodization of copper foil and copper-coated Kapton substrates, in sodium sulphide electrolyte, copper sulphides with a nanowall nanostructure were obtained (Fig. 4).⁶⁰ The sample anodized with 1.5 V at 5 °C exhibited the highest methane formation in the CO_2PR (Table 1 entry 5) under the irradiation of simulated sunlight. At low voltage and temperature, sulphur diffusion was low, leading to a lower concentration of excess sulphur in the sample that yielded Cu_2S . As a result, less bulk Cu vacancy defects were formed within the sample. Cu_2S exhibited higher charge mobility than the CuS nanostructured array, which was obtained at high temperature and high voltage.

To engineer the bandgap energy of the photocatalyst that matches the solar spectrum, a solid solution with large and small bandgap semiconductors was proposed. For instance, Arai *et al.* used the Cu-based sulphide complex $\text{Cu}_2\text{ZnSnS}_4$ with a direct bandgap of 1.5 eV and a large optical absorption coefficient and obtained a high selectivity of the photoelectrochemical CO_2 reduction reaction (>80%).⁶⁸ The Cu-based sulphide complex reported by Liu *et al.* showcased that the Cu-based sulphide complex was able to reduce CO_2 under visible light irradiation in the presence of a Ru co-catalyst.⁶⁹ The $\text{Ru-Cu}_x\text{Ag}_y\text{In}_z\text{Zn}_k\text{S}_m$ solid solutions induced the formation of methanol in CO_2PR under visible light irradiation (Table 1 entry 6). Although the study reported that the optimal performance could be obtained through the elemental composition manipulation, the nanostructures of the sulphide complex were not revealed. It is therefore questionable whether the efficiency of these photocatalysts could be further enhanced through the manipulation of their microstructures. Moreover, the stability of metal sulphates in most of the studies has not been demonstrated, and this should be emphasized more in future work.

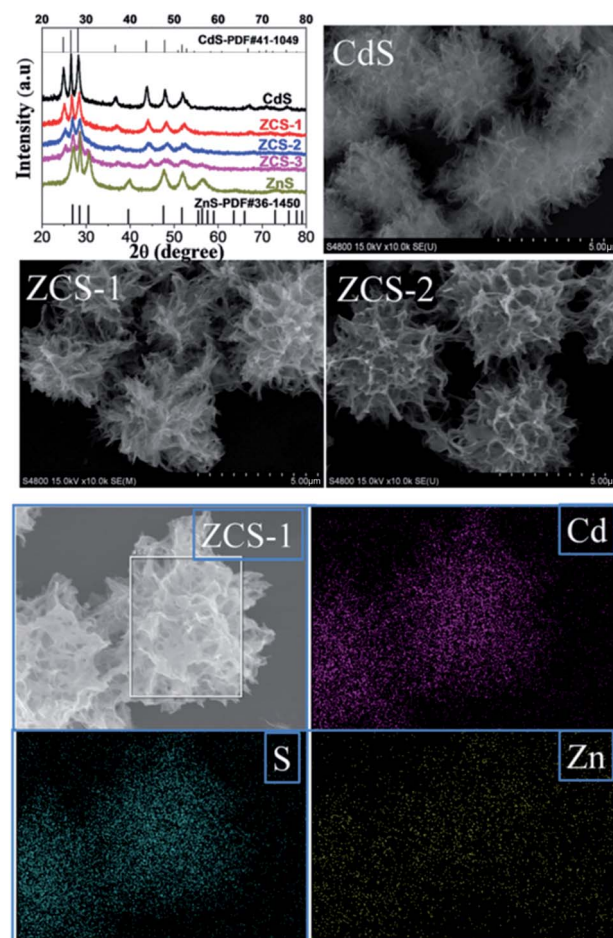


Fig. 3 XRD patterns, SEM images and EDX mapping of the synthesized CdS and $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ solid solutions. Reproduced from ref. 58 with permission.

2.2 Oxides

Semiconducting oxides have been widely used as photocatalysts because of their stability and resistance to photocorrosion under irradiation. Hence, oxides have been used for photooxidation and photoreduction reactions. The intrinsic properties of metal oxides play a critical role in determining their feasibility for CO_2PR . For example, CO_2PR was observed for p-type NiO covalently linked with a Zn porphyrin light-harvesting sensitizer and rhenium bipyridine system, whereas the CO oxidation reaction was observed when a similar system was coupled with n-type NiO.⁷⁰ There are two main groups of metal oxides with a closed-shell electronic configuration that have been at the centre of interest for a CO_2PR system. The first group includes octahedrally coordinated d^0 transition metal ions (Ti^{4+} , Zr^{4+} , Nb^{5+} , Ta^{5+} , V^{5+} , and W^{6+}). Apart from TiO_2 , which is the most prominent member of this group, other binary oxides (e.g., ZrO_2 , Nb_2O_5 , and Ta_2O_5) have been used in CO_2PR . A number of more complex oxides referred to as titanates, niobates, tantalates, *etc.*^{71,72} are often found in a perovskite composite, AMO_3 (A = electropositive cation and M = transition metal; e.g., SrTiO_3 and NaNbO_3), or in perovskite-related structures. Since



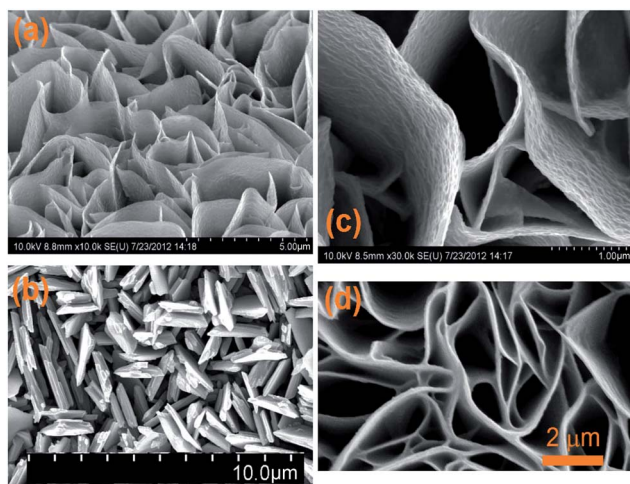


Fig. 4 SEM images of the copper sulphide nanowalls oriented vertically to the copper foil anodized at 1.5 V at room temperature (a and c), and 3.0 V (b) and 1.5 V (d) at 5 °C. Reproduced from ref. 60 with permission.

a recent published review has covered the use of perovskite oxide nanomaterials for CO₂ photoreduction,⁷³ this area will not be further discussed here. The second group includes main group metal oxides in a d¹⁰ configuration with a general formula of M_yO_z or A_xM_yO, where M represents Ga, Ge, In, Sn, or Sb. Many of these photocatalytically active binary and ternary oxides initially found application in photocatalytic water splitting, but they have very recently started to be utilised for CO₂PR.⁷³

Zinc-based materials. ZnO has been widely used in the photodegradation of organic dyes and chemicals due to its direct and wide bandgap (3.37 eV).¹⁰³ Additionally, the bandgap and photocatalytic mechanism of ZnO are similar to those of TiO₂, and thus, ZnO was also used for CO₂PR. To compare the CO₂ photoreduction efficiency of ZnO with that of other commonly used wide bandgap semiconductors, Yahaya *et al.* employed commercially available TiO₂, ZnO and NiO as photocatalysts for CO₂ photoreduction under 355 nm UV laser irradiation.⁷⁴ Among the samples, ZnO and NiO produced high yields of methanol (325 and 388 μmol g⁻¹ h⁻¹ over 1.5 h, respectively, Table 1, entries 7 and 8); whereas TiO₂ had the lowest production yield. In order to enhance the light absorption of commercial ZnO in the UV-vis region, ZnO was calcined to 350 °C and the ZnO obtained was immobilised onto a stainless-steel mesh to reduce the agglomeration of the photocatalyst.¹⁰⁴ The maximum conversion of CO₂ achieved was 11.9% (*i.e.*, percentage of CH₄ produced from CO₂ in the presence of a CH₄ reductant). A study revealed that the microstructure of ZnO played a more vital role than doping of ZnO with nitrogen (N-ZnO), even though the latter showed enhanced light absorption from 400 to 650 nm.⁷⁵ A fluffy mesoporous structured ZnO with a surface area of 29.7 m² g⁻¹ exhibited enhanced CO production (0.73 μmol g_{catalyst}⁻¹ h⁻¹, Table 1, entry 9) under UV-vis light irradiation when compared to the N-doped ZnO (1.2 m² g⁻¹, 0.04 μmol g_{catalyst}⁻¹ h⁻¹, Table 1, entry 10). A separate publication reported that ZnO plates with

porous rectangular and assembled hexagonal morphologies (15.5 m² g⁻¹, which was about 2.6 times that of the commercial ZnO, Fig. 5) could be obtained by using NH₄Zn₃(OH)₆NO₃.⁷⁶ The synthesized ZnO plates exhibited a much higher production of CO and CH₄ (76.35 and 20.52 ppm h⁻¹, respectively) than the pristine hexagonal ZnO plates (44.68 and 1.57 ppm h⁻¹ of CO and CH₄, respectively).

Doping has been widely used to extend the light absorption of wide bandgap semiconductors to a longer wavelength region by introducing intra-band states above the valence band. However, this approach tends to increase the recombination rate and decrease the charge mobility of the semiconductor, as discussed in Section 1. To avoid these drawbacks, the introduction of foreign cations into the binary semiconductor was considered instead of doping. For example, the ternary Zn₂GeO₄ semiconductor was used for CO₂PR under UV-vis irradiation. By fabricating ultralong and ultrathin single crystal Zn₂GeO₄ nanoribbons, the photocatalytic reduction rate of CO₂ into CH₄ was greatly enhanced to 25.0 μmol g_{catalyst}⁻¹ h⁻¹ when compared to that of the bulk Zn₂GeO₄ (trace amounts, Table 1, entry 12).⁷⁷ The enhanced photocatalytic efficiency was attributed to the superb crystal quality and higher surface area (28.3 m² g⁻¹) when compared to the bulk Zn₂GeO₄ (0.75 m² g⁻¹), resulting in enhanced separation of photogenerated electron-hole pairs and charge mobility. In the following year, the same group proposed the synthesis of the single crystal Zn₂GeO₄ at 40 °C to optimise the surface area.⁷⁸ As a result, the surface area of the synthesized Zn₂GeO₄ nanorods was 33.1 m² g⁻¹ which yielded 179 and 35 ppm g_{catalyst}⁻¹ h⁻¹ of CO and CH₄, respectively. Further increasing the temperature to 100 °C, however, decreased the surface area to 14.8 m² g⁻¹, yielding only 3.2 and 0.4 ppm h⁻¹ of CO and CH₄, respectively. By reducing the concentration of the Ge-precursor and the solvothermal time employed in the first study in 2010 (refer to ref. 77) by half, a sheaf-like superstructured Zn₂GeO₄ was obtained and reported by the same group in 2012 (Fig. 6).⁷⁹ Although the CO₂PR of the superstructured Zn₂GeO₄ was not reported in this study, the optimised RuO₂ and Pt co-loaded Zn_{1.7}GeN_{1.8}O nano-sheaves after nitridation (32.33 m² g⁻¹) could produce CH₄ with an apparent quantum yield of 0.024% at 450 nm (Table 1 entry 14).

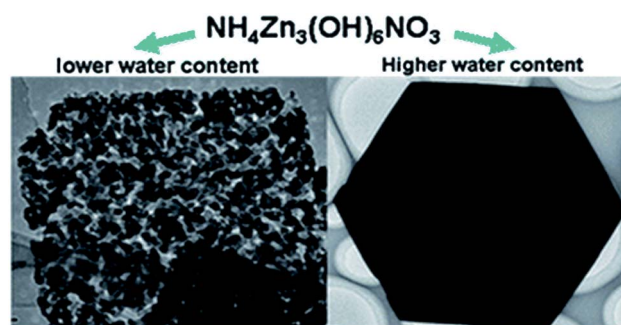


Fig. 5 ZnO synthesized from NH₄Zn₃(OH)₆NO₃ with <3 mL (left) and >3 mL (right) of water. Reproduced from ref. 76 with permission.



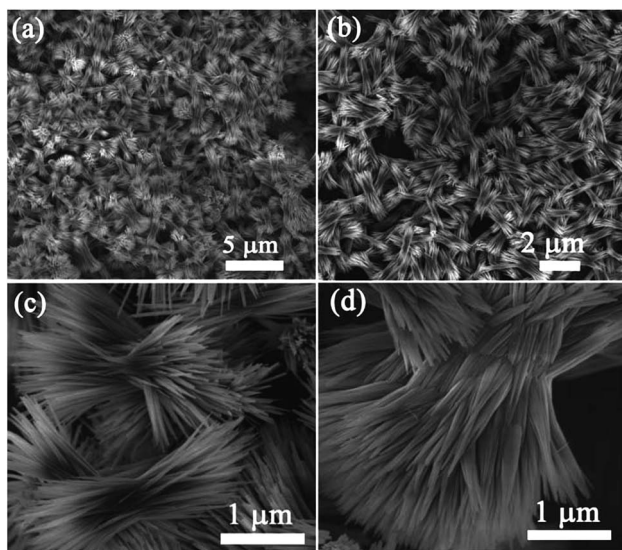


Fig. 6 SEM images of a sheaf-like Zn_2GeO_4 superstructure at different magnifications. Reproduced from ref. 79 with permission.

Other nanostructured ternary Zn-based oxides were also proposed by the same group more recently, including ZnGa_2O nanosheet-scaffolded microspheres⁸⁰ and hexagonal nanoplate-textured Zn_2SnO_4 with micro-octahedron architecture for CO_2 PR application.⁸¹ The unique architecture of the synthesized ZnGa_2O and Zn_2SnO_4 significantly enhanced the separation of photogenerated electron-hole pairs, increased the surface area and extended light absorption. Hence, the methane yield obtained from the CO_2 PR was greatly improved from trace amounts to 69 and 47 ppm $\text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ for the nanostructured ZnGa_2O and Zn_2SnO_4 , respectively (Table 1, entries 15 and 16).

To promote co-adsorption of CO_2 and H_2O , Guo *et al.* fabricated ZnFe_2O_4 spinels doped with Ce.⁸² By using *in situ* FTIR, it was found that the CO_2 amount adsorbed on the surface of Ce-doped ZnFe_2O_4 was much higher than that on pristine ZnFe_2O_4 . This phenomenon was attributed to the increase of basicity due to the presence of alkaline CeO_2 and electron density on the surface of the Ce-doped ZnFe_2O_4 , thereby increasing the number of adsorption bonds between the CO_2 molecules and the surface of the photocatalyst, and activating the O=C bond (Fig. 7). The formation of active b-CO_3^{2-} and b-HCO_3^- species, which could be readily translated to highly valuable products in the CO_2 photoreduction, was detected. Recently, Xiao *et al.* discovered that ultrafine ZnFe_2O_4 nanoparticles with a high specific surface area ($112.9 \text{ m}^2 \text{ g}^{-1}$) could promote the selectivity of the photoproduction of CH_3CHO over $\text{CH}_3\text{CH}_2\text{OH}$, and they produced 57.8 and $13.7 \mu\text{mol g}^{-1} \text{h}^{-1}$, respectively, under visible light irradiation ($>400 \text{ nm}$).¹⁰⁵

Tungsten-based materials. Among the first group of metal oxides, WO_3 has the smallest bandgap energy of 2.7 eV and as the edge of its conduction band is located at 0 V vs. NHE at pH 7, it cannot reduce CO_2 .^{4,106} However, Xie *et al.* found that when the architecture of the WO_3 changed from quasi-cubic with an equal percentage of $\{002\}$, $\{200\}$ and $\{020\}$ facets to rectangular sheet-like with dominant $\{002\}$ facets, it could induce CO_2 PR in

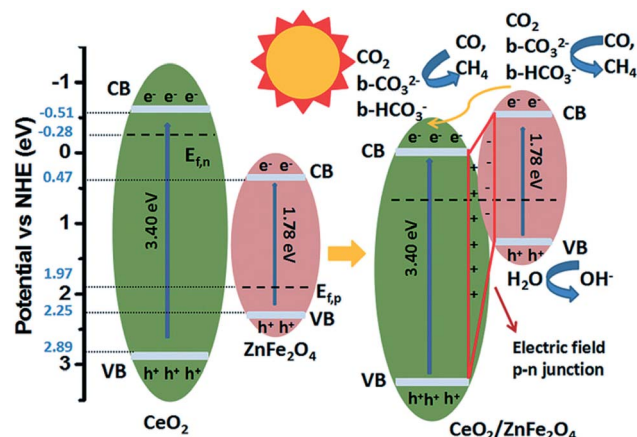


Fig. 7 Schematic of the mechanism of CO_2 photoreduction with H_2O vapour over $\text{CeO}_2/\text{ZnFe}_2\text{O}_4$. Reproduced from ref. 82 with permission.

the presence of H_2O .⁸³ The change of the predominantly exposed facets had a significant effect on the electronic configuration of WO_3 , in which the rectangular sheet-like WO_3 possessed a slightly larger bandgap (2.79 eV) and its conduction band was increased by 0.3 eV. As a result, the conduction band was positioned slightly above the CH_4/CO_2 potential (-0.24 V), inducing the methane formation from CO_2 at a rate of $\sim 0.34 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$. Chen *et al.* found that the conduction band of WO_3 was shifted to a more negative position (-0.42 V , bandgap energy: 2.79 eV) with a stronger reducing driving force, when the ultrathin ($\sim 4\text{--}5 \text{ nm}$) single crystal WO_3 was synthesized using a solid-liquid phase arc discharge route in an aqueous solution.⁸⁴ The yield obtained from the CO_2 PR was $\sim 1.1 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ under visible light irradiation ($\lambda > 420 \text{ nm}$), whereas commercial WO_3 powder produced only trace amounts of methane under the same conditions. A high aspect ratio of ultrathin $\text{W}_{18}\text{O}_{49}$ exhibited extended optical properties in the visible and near infrared regions due to the presence of a large amount of oxygen vacancies (Fig. 8).⁸⁵ The synthesized

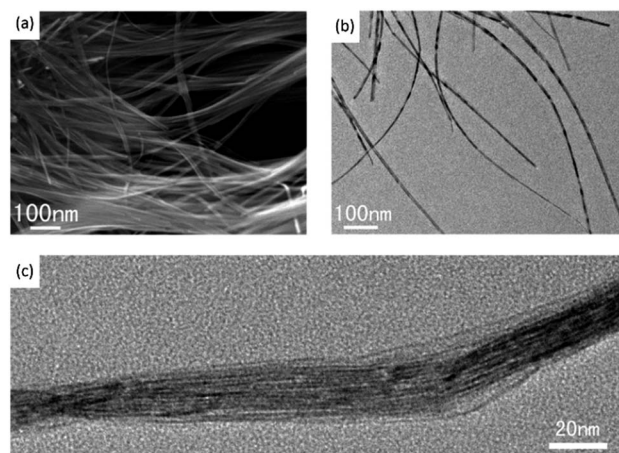


Fig. 8 SEM (a), TEM (b) and high resolution TEM (c) images of $\text{W}_{18}\text{O}_{49}$. Reproduced from ref. 85 with permission.



ultrathin $W_{18}O_{49}$ exhibited the photoreduction of CO_2 to CH_4 at $70^\circ C$ under visible light irradiation without a co-catalyst (Fig. 8, Table 1 entry 20). The study observed that the selectivity towards CH_4 over other hydrocarbons (*e.g.*, ethanol and acetone) was as high as 95%.

The introduction of foreign elements into tungsten oxide, which generated ternary Bi_2WO_6 , was reported.⁸⁶ The Bi_2WO_6 with predominant $\{001\}$ facets was proposed to be the most energetically favoured reactive surface for CO_2 dissociation, resulting in $1.1 \mu mol g_{catalyst}^{-1} h^{-1}$ of methane under visible light irradiation ($\lambda > 420 nm$), whereas the bulk Bi_2WO_6 prepared through a solid state reaction produced only trace amounts of methane. Cheng *et al.* also proposed that the microstructure of Bi_2WO_6 could enhance CO_2 adsorption.⁸⁷ A template-free anion exchange strategy was used to synthesize hollow microspheres of Bi_2WO_6 (Fig. 9a and b). The synthesized Bi_2WO_6 exhibited higher CO_2 adsorption capacity when compared to $BiVO_4$ and $BiPO_4$ nanoparticles without hollow structures (Fig. 9c and d, respectively), leading to high photo-conversion of CO_2 into methanol.

Niobate-based materials. Niobates with a perovskite structure have gained some attention because they share many characteristics (*i.e.*, non-toxicity, stability, and indirect wide bandgap) with titanates. Moreover, the conduction band of niobates is slightly more reductive than that of titanates, suggesting that niobates could be a more suitable material for CO_2 PR. A study had shown that the microstructure of $NaNbO_3$ played an important role in its photocatalytic activity. $NaNbO_3$ nanowires ($653 ppm h^{-1} g^{-1}$, Fig. 10a) with a smaller bandgap (3.2 eV) and larger surface area ($12.0 m^2 g^{-1}$) exhibited much higher methane formation from CO_2 when compared to the $NaNbO_3$ bulk (3.2 eV, $1.4 m^2 g^{-1}$, $22 ppm h^{-1} g^{-1}$, Fig. 10b).⁸⁸ The enhanced photocatalytic activity was proposed to be due to the high crystallinity, high aspect ratio and anisotropic effect of the synthesized nanowires. Li *et al.* also demonstrated that the size and microstructure of photocatalysts play an important role in their photocatalytic activity.⁸⁹ KNb_3O_8 and HNb_3O_8

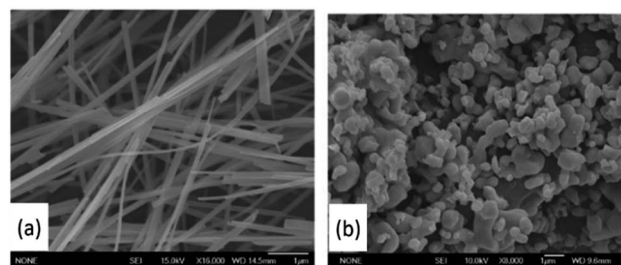


Fig. 10 $NaNbO_3$ nanowires (a) and bulk particles (b). Reproduced from ref. 88 with permission.

nanobelt samples with a higher surface area, which were 28.8 and $39.4 m^2 g^{-1}$, respectively, exhibited a ≥ 10 times higher photoproduction rate of methane from CO_2 than the irregularly shaped KNb_3O_8 and HNb_3O_8 samples, which were 2.7 and $6.5 m^2 g^{-1}$, respectively (Table 1 entry 24 and 25). A similar observation was reported by Xie *et al.*, in which the nanoplates of $SrNb_2O_6$ with an increased surface area revealed improved chemisorption of CO_2 and the separation of photogenerated electron-hole pairs.¹⁰⁷ As a result, more products, such as CO and CH_4 , were obtained from the CO_2 PR compared to the $SrNb_2O_6$ nanorods and nanoparticles with a lower surface area. A more recent study revealed that the nanorod-structured $SrNb_2O_6$ ($1.78 m^2 g^{-1}$, $51.2 \mu mol g_{catalyst}^{-1} h^{-1}$) exhibited a higher photoreduction rate and selectivity towards CO evolution over H_2 ($>95\%$) than the $SrNb_2O_7$ nanoflakes ($3.85 m^2 g^{-1}$, $6 \mu mol g_{catalyst}^{-1} h^{-1}$, $\sim 39\%$) and $SrNb_2O_6$ nanoparticles even though the latter possessed a higher surface area.⁹⁰ This phenomenon was attributed to the separation of the reduction and oxidation sites on the nanorods that decreased the recombination of photogenerated electron-hole pairs.

Tantalum-based materials. Tantalum-based semiconductors have been widely used as a photocatalyst for water splitting. Having higher potentials than TiO_2 and above the reduction potential of CO_2/CH_3OH , H_2CO_3/CH_3OH , HCO_3^-/CH_3OH and CO_3^{2-}/CH_3OH , Ta_2O_5 can be employed for the CO_2 PR.⁹² However, the large bandgap energy of Ta_2O_5 ($\sim 3.9 eV$) has restricted its light absorption in the visible region.¹⁰⁸ Hence, Sato *et al.* used $N-Ta_2O_5$ to couple a series of ruthenium bipyridine catalysts for the photocatalytic CO_2 reduction to formic acid under visible light irradiation ($405 nm$).¹⁰⁹ The production rate was found to be $\sim 70 \mu mol g_{catalyst}^{-1} h^{-1}$ in an acetonitrile/triethanolamine mixture. To enhance the electron transportation and suppress the electron-hole recombination, Ta_2O_5 was immobilised on reduced graphene and NiO_x was used as the co-catalyst (Fig. 11).⁹¹ The highest photoproduction rate of methanol from 3% $NiO_x-Ta_2O_5-1\%$ reduced graphene sample was ~ 20.83 and $197.92 \mu mol g_{catalyst}^{-1} h^{-1}$ without and with the presence of $NaHCO_3$ solution, respectively.

Much effort has focused on $InTaO_4$ as the ternary tantalum-based semiconducting photocatalyst for CO_2 PR. For instance, Pan and Chen demonstrated that $InTaO_4$ could reduce CO_2 to methanol ($\sim 1.1 \mu mol g_{catalyst}^{-1} h^{-1}$) in $0.2 M KHCO_3$ aqueous solution under visible light irradiation.¹¹⁰ The methanol production rate could marginally increase to $1.2 \mu mol g_{catalyst}^{-1}$

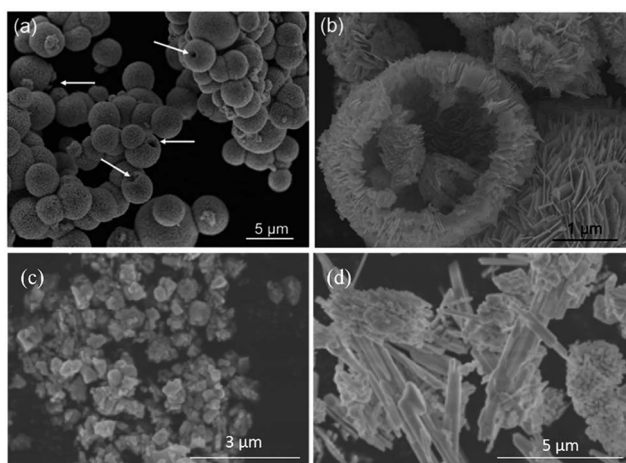


Fig. 9 SEM images of Bi_2WO_6 hollow microspheres (a and b), $BiVO_4$ (c) and $BiPO_4$ (d) reproduced from ref. 87 with permission.



h^{-1} after coupling 1 wt% NiO as the co-catalyst and $1.4 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ after the application of reduction–oxidation pre-treatment. Tuning the size and crystallinity of InTaO_4 nanoparticles resulted in the bandgap energy range from 2.6 to 3.0 eV and could also enhance the production of methanol from CO_2 .¹¹¹ The highest production rate was about $2.7 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ when 1.0 wt% NiO was added as the co-catalyst. The methanol generation from InTaO_4 was further enhanced by introducing core–shell Ni/NiO nanoparticles on nitrogen doped InTaO_4 , leading to $160 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ under the irradiation of light with wavelengths ranging from 390 to 770 nm.⁹² KTaO_3 was also used to reduce CO_2 to CO under visible light irradiation.¹¹² Three samples were synthesized with different bandgaps ranging from 3.5 to 3.7 eV and yielded the highest amount of CO at $\sim 62 \text{ ppm g}_{\text{catalyst}}^{-1} \text{h}^{-1}$.

Recently, $\text{LaTa}_7\text{O}_{19}$ and $\text{CaTa}_4\text{O}_{11}$ (bandgap energies of 4.1 and 4.5 eV, respectively) were shown to be active for CO_2 PR. CO was produced after loading with 1 wt% Ag co-catalyst due to the preferable conduction band positions (50 and $70 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$, respectively, in the presence of 0.1 M NaHCO_3 under the irradiation of a 400 W high-pressure mercury lamp).⁹³ NaTaO_3 doped with different elements, such as Mg, Ca, Sr, Ba and La, has been proposed as a highly active photocatalyst for CO_2 PR using water as the electron donor in the presence of a Ag co-catalyst under UV irradiation.⁹⁴ Among the samples, Ba-doped NaTaO_3 loaded with 1.0 wt% Ag co-catalyst using the liquid-phase reduction method exhibited the highest CO production and selectivity from CO_2 ($\sim 50 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$ and 56%, respectively).

Quaternary tantalates have been developed recently and revealed to be active for CO_2 photoreduction in the presence of water.¹¹³ $\text{K}_2\text{RETa}_5\text{O}_{15}$ (RE = rare-earth element, namely La, Ce, Pr, Nd, Y, and Sm) was fabricated using the flux method with KCl, which favoured the rod-like morphology, followed by calcination treatment at $1150 \text{ }^\circ\text{C}$ for 6 h.⁹⁵ Among the quaternary tantalates, $\text{K}_2\text{CeTa}_5\text{O}_{15}$ possessed the smallest bandgap energy (2.42 eV, $0.7 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$), but $\text{K}_2\text{YT}_5\text{O}_{15}$ photo-produced the highest amount of CO (3.86 eV, $91.9 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$). The addition of Y was shown to be beneficial for capturing CO_2 and subsequently for photoreduction. Meanwhile, the presence of K in the tantalates played an important role in determining the growth orientation of the rod-like structure, thereby affecting the activity in CO_2 photoreduction.

Miscellaneous. CeO_2 is a basic metal oxide that can transform inert linear CO_2 to b-HCO_3^- and b-CO_3^{2-} to reduce the reductive potential of CO_2 .¹¹⁴ Hence, it has recently attracted a lot of attention. However, it suffers from rapid recombination of photogenerated electron–hole pairs and possesses a large bandgap (3.0–3.4 eV), which restricts the light absorption in the UV range.¹¹⁵ To improve the performance of CeO_2 for the photocatalytic reduction of CO_2 under visible irradiation, Xiong *et al.* proposed the coupling of $\text{Ag}/\text{Ag}_3\text{PO}_4$ with CeO_2 to construct heterojunctions for enhancing the separation of photogenerated electron–hole pairs and improve light absorption because Ag_3PO_4 has a narrow bandgap of 2.42 eV.¹¹⁶ The highest CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ yield obtained was 10.6 and $7.9 \mu\text{mol g}_{\text{catalyst}}^{-1} \text{h}^{-1}$, respectively. Zhang discovered that when Ni

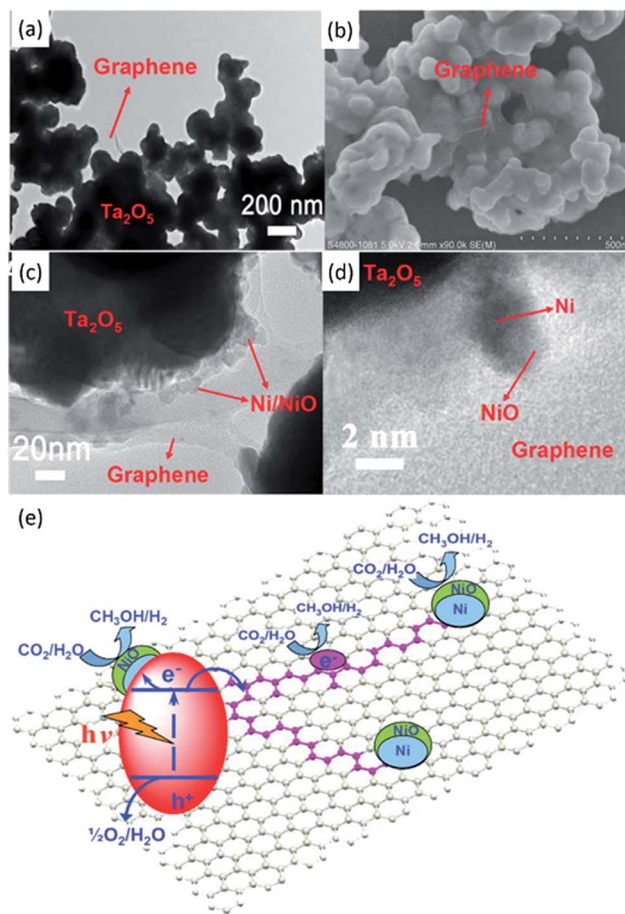


Fig. 11 TEM (a) and SEM (b) images of Ta_2O_5 immobilised on reduced graphene. TEM (c) and SEM (d) images of the NiO_x - Ta_2O_5 -reduced graphene composite. Schematic illustration of the charge separation and transfer in the Ta_2O_5 -reduced graphene system under UV-vis light (e). Reproduced from ref. 91 with permission.

was loaded on CeO_2 , the nanocomposite exhibited enhanced photo(thermo)catalytic performance and inhibited carbon deposition.¹¹⁷ Moreover, it is interesting to note that the full light spectrum response from UV to infrared of the Ni metal on CeO_2 decreased the activation energy of C and CH oxidation steps, thus improving the overall photo(thermo)catalytic performance.

MgO was employed to photocatalytically reduce CO_2 into CO with a production rate of $\sim 1.6 \mu\text{mol g}^{-1} \text{h}^{-1}$ over 6 h in the presence of H_2 as the reductant under UV light ($\lambda < 290 \text{ nm}$).¹¹⁸ Mesoporous Ga_2O_3 yielded 1.46 and $0.21 \mu\text{mol g}^{-1} \text{h}^{-1}$ of CO and CH_4 , respectively, from CO_2 under visible light irradiation.¹¹⁹ When Ga_2O_3 was loaded with Ag, the photoproduction rate of CO from CO_2 was $10.5 \mu\text{mol g}^{-1} \text{h}^{-1}$ under UV light irradiation (Table 1 entry 33).⁹⁶ Iron oxides were proposed as a photoactive centre to induce the photocatalytic reduction of CO_2 .¹²⁰ Using electron spin resonance spectroscopy (ESR), the photogenerated electrons from the Fe–O species were efficiently consumed by CO_2 under UV irradiation.

Lamellar BiVO_4 was proposed to exhibit a selective methanol production from CO_2 photoreduction under visible light



irradiation.⁹⁷ The maximum CH₃OH production rate was 5.52 μmol h⁻¹ when 0.2 g of BiVO₄ was suspended in 100 mL of NaOH (1.0 M) under full spectrum irradiation of a Xe lamp. The photocatalytic mechanism was proposed according to which the Bi³⁺ sites could efficiently receive electrons from the V 3d-block bands of the BiVO₄ to form CO₂^{•-} radical anions, leading to the formation of methoxyl radicals (·OCH₃) and eventually CH₃OH after hydrogen abstraction. Wang *et al.* doped the atomically thin layers of BiVO₄ with different percentages of Co.¹²¹ The Co-doped BiVO₄ exhibited an efficient and stable activity for CO₂ photoreduction to CH₄. The optimal CH₄ production rate was 23.8 μmol g⁻¹ h⁻¹, which was three times higher than that of the pristine BiVO₄, at 60 °C with an atmospheric CO₂ concentration (~400 ppm) under a UV lamp (25 W at 254 nm). The enhancement of the production rate of the Co-doped BiVO₄ was suggested to be due to the presence of electron enriched adsorption sites, which was contributed by the Co dopant, activating the CO₂ molecules for further reduction reaction.

Delafossite materials with a general stoichiometry of ABO₂, in which A is a monovalent metal ion, such as Cu, Ag, and Pt, and B is a trivalent metal ion, such as Al, Ga, and Fe, as the new class of photocatalysts have also been considered for CO₂PR.⁹⁸ CuGaO₂ (bandgap energy ~3.7 eV and weak absorption at 2.6 eV) and the Fe-alloyed CuGa_{1-x}Fe_xO (1.5 eV) facilitated the photo-generation of CO from CO₂ under the irradiation of a Xe lamp though varied amounts of Fe substituted into CuGaO₂ did not significantly enhance the CO₂ photoreduction performance (Table 1 entry 35).⁹⁸

Based on the Lewis acidity of CO₂, alkaline catalysts will benefit the adsorption and activation of CO₂. Layered double hydroxide (LDH) materials usually possess high specific surface areas, which provide numerous active sites for the catalytic reaction. The fabricated CoAl LDH facilitated an enhanced CO₂ photoreduction reaction when compared to P25 due to the surface alkaline OH groups for efficient adsorption of CO₂ at a low concentration.⁹⁹ The utilisation of LDH in CO₂ photoreduction has been reviewed previously, and thus, interested readers may refer to the published review articles.^{40,122}

In summary, metal oxides have shown their ability to promote photocatalytic reduction of CO₂, as discussed in the previous section. However, most of these photocatalysts only work under UV irradiation due to their large bandgap energies (>3 eV). The relatively large bandgap of metal oxides originates from the valence band maximum, which is formed by O 2p orbitals and is more positive than 3 V.¹²³ Hence, if metal oxides meet the thermodynamic requirement for CO₂PR and H₂O photooxidation, then the bandgap of the metal oxides inevitably becomes larger than 3.0 eV, which is too wide to absorb visible light.¹²⁴

2.3 Oxynitrides

Tantalum-based materials. The N 2p orbital has a higher potential energy than the O 2p orbital, which indicates that metal oxynitrides as well as metal nitrides could be employed as an efficient photocatalyst.^{42,125} For example, in the case of

tantalum oxynitride and tantalum nitride, when nitrogen-based N 2p atomic orbitals were introduced into Ta₂O₅, new orbitals with a higher bound state energy are generated, resulting in a decrease of bandgap energy.^{42,108,126} As a result, the bandgaps of TaON and Ta₃N₅ (2.5 and 2.1 eV, respectively) are both smaller than that of Ta₂O₅ (3.9 eV) and thus can effectively absorb visible light and drive the photocatalytic activity. Moreover, the N content plays an important role in determining the bandgap energy in oxynitrides and nitrides. Therefore, Gao *et al.* proposed a Ca-assisted urea synthesis method to controllably synthesise TaON and Ta₃N₅ with a tailored N composition.¹²⁷ In addition, the initial urea : Ta molar ratio used in the proposed synthesis method was also beneficial to control the size and homogeneity of the final product. Recently, the use of the porous spherical architecture of TaON for CO₂ photoreduction was proposed.¹⁰⁰ The surface area of the porous spherical TaON was ~11.12 m² g⁻¹, whereas that of commercial TaON was ~7.41 m² g⁻¹. As a result, the CH₃CHO and C₂H₅OH production rates from CO₂ using the porous TaON (0.52 and 2.03 μmol g_{catalyst}⁻¹ h⁻¹) were higher when compared to those of the commercial TaON (0.16 and 0.84 μmol g_{catalyst}⁻¹ h⁻¹) under visible light irradiation. The enhanced CO₂PR in the porous TaON was attributed to the increase of surface area. In addition, the reduction of charge transfer distance and enhanced light scattering within the porous spherical structure were also suggested to play roles in enhancing the photocatalytic reduction of CO₂.

The CO₂PR is a multi-electron process, and a variety of products can be produced using a single semiconducting photocatalyst. The achievement of efficient and selective production of highly valuable fuels is critical for viable CO₂ photoreduction processes. The application of perovskite oxynitrides, such as CaTaO₂N coupled with the binuclear Ru(II) complex photosensitiser and loaded with the Ag co-catalyst, revealed an enhanced selectivity for HCOOH production (>99%) from CO₂ under visible light irradiation due to the enhanced interfacial electron transfer.¹²⁸ A similar approach with the same photosensitiser and co-catalyst coupled with yttrium-tantalum oxynitride (YTON) was recently proposed by the same group.¹²⁹ The YTON (2.1 eV) exhibited a smaller bandgap than CaTaO₂N (2.5 eV), thus extending the light absorption up to 600 nm. Moreover, the selectivity for HCOOH formation from CO₂ was not affected and remained as high as that in their previous study (>99%).

Zinc-based materials. Mesoporous ZnGeON was used as a photocatalyst for CO₂PR under visible light irradiation (λ < 400 nm).¹³⁰ The prolonged nitridation time from 1 to 15 h decreased the Zn and O contents, in which Zn was evaporated and O was substituted by N, at 800 °C in an NH₃ environment. However, the crystallinity of ZnGeON was enhanced with a slight decrease in the surface area. The ZnGeO nitrided for 10 h (24.4 m² g⁻¹) exhibited the highest CH₄ production rate of 2.7 ppm g_{catalyst}⁻¹ h⁻¹, which was higher than those of the ZnGeON prepared using the solid-state reaction (3.3 m² g⁻¹, 1.1 ppm g_{catalyst}⁻¹ h⁻¹) and N-doped TiO₂ (2.2 ppm g_{catalyst}⁻¹ h⁻¹). As discussed in Section 2.2, zinc-based materials like ZnGa₂O₄ possessed a bandgap energy of ~4.5 eV, in which



the valence band was mainly composed of O 2p and the conduction band was formed from the hybridization of Ga 4s and Zn 4p orbitals.^{80,101} In order to reduce the bandgap energy, nitridation of mesoporous ZnGa₂O₄ was proposed. The nitridation of ZnGa₂O₄ stimulated the hybridization of Zn 3d, N 2p and O 2p and formed the valence band, whereas the conduction band was composed of the Ga 4s and 4p orbitals.¹⁰¹ As a result, the bandgap energy was reduced to 2.5 eV, resulting from the uplifting of the maximum of the valence band and lowering of the minimum of the conduction band. To further enhance the CO₂PR performance, a ZnGa₂ON solid solution was modified with ZnAl₂O₄ that acted as the CO₂ arrester (Fig. 12).¹⁰¹ The increase of Zn content had also decreased the bandgap energy to 2.3 eV. Benefiting from the mesoporous structure, smaller bandgap and enhanced CO₂ adsorption ability, the ZnAl₂O₄-modified ZnGa₂ON showed a methane generation rate of 9.2 μmol g_{catalyst}⁻¹ h⁻¹ from CO₂, which was 9 times higher than that of the pristine ZnGa₂ON under visible light irradiation (λ ≥ 420 nm).

2.4 Nitrides

Gallium-based materials. Through engineering the nanostructure of the co-catalyst used, selectivity using semiconducting nitrides could be enhanced dramatically, as demonstrated by AlOtaibi *et al.*¹⁰² The decoration of the non-polar GaN nanowires with the Rh core and amorphous Cr₂O₃ shell co-catalyst significantly increased the production rate of CH₄ from 1.3 (bare GaN) to 3.5 μmol g_{catalyst}⁻¹ h⁻¹, but the CO production rate decreased from 1130 (bare GaN) to ~120 μmol g_{catalyst}⁻¹ h⁻¹ in 24 h (Fig. 12). Due to the effective collection of photogenerated electrons by the Rh core and amorphous Cr₂O₃ shell co-catalyst, no apparent reductive reaction (*e.g.*, photoreduction of CO₂ to CO) occurred on the surface of GaN without Rh coverage. As a result, the product selectivity towards CH₄ was enhanced in the CO₂PR under UV-visible light irradiation. In addition, the decoration of the GaN nanowires with Rh/Cr₂O₃ could suppress the back reaction that formed H₂O from H₂ and O₂, and offered adsorption sites for CO₂.

In summary, both metal oxynitrides and nitrides have shown their capability to photoreduce CO₂ with more favourable optical properties when compared to metal oxides. Unfortunately, these groups of materials have not been extensively explored.

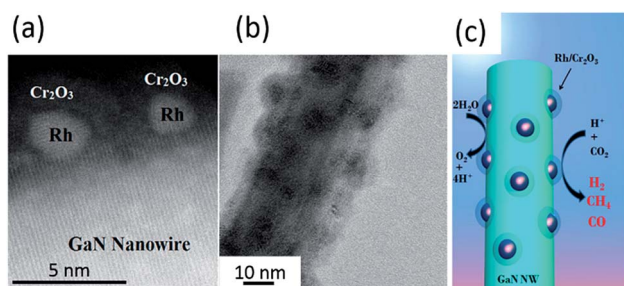


Fig. 12 (a) High-resolution TEM image and (b) TEM image of Rh/Cr₂O₃ core/shell decorated GaN nanowires. (c) Schematic of the photoreduction processes of CO₂ on Rh/Cr₂O₃-decorated GaN nanowires. Reproduced from ref. 102 with permission.

3. Hole scavengers for CO₂ photoreduction

Various semiconducting materials have been proposed as photocatalysts for CO₂PR under UV and/or visible irradiation, as discussed in Section 2 and summarised in some other references.^{7–10,103,131} However, the quantum efficiency of the CO₂ photo-conversion into hydrocarbons remained low and could not rely only on the development of photocatalysts. System optimisation plays an important role in optimising the conversion rate and selectivity as well as photocatalyst stability. Therefore, the increase of CO₂PR efficiency through the introduction of a hole scavenging agent has gained significant interest. In this section, the use of organic and inorganic hole scavengers is reviewed.

3.1 Inorganic hole scavengers

As discussed in Section 2.1, metal sulphides suffer from photocorrosion in an aqueous dispersion due to the oxidation of lattice S²⁻ ions to elemental S and subsequently to sulphates.⁵¹ Hence, the addition of reducing agents to prevent the oxidation of the lattice S²⁻ ions by scavenging the photogenerated holes was proposed. Kanemoto *et al.* achieved a cumulative quantum yield of 72% with irradiation of UV light at 313 nm (*i.e.*, 75.1 and 1.7 μmol g_{catalyst}⁻¹ h⁻¹ of HCOOH and CO, respectively) when NaH₂PO₂ and Na₂S (0.35 and 0.24 M, respectively) were added into the system that contained ZnS as the photocatalyst for CO₂PR (Table 2 entry 1).¹³²

A systematic study was recently carried out to investigate the effect of Na₂S as the hole scavenger for ZnS on the CO₂PR at λ = 345 nm.¹³³ The study elucidated that the photogenerated holes on the surface of ZnS were directly consumed by Na₂S, whereas photogenerated electrons were pumped into the conduction band simultaneously. In addition, the behaviour of the reaction rate at different pH values resembled that of the solubility of CO₂, discarding the direct participation of the HCO₃⁻ and CO₃²⁻ in the photoreduction process. This observation was supported by a very recent study, in which KHCO₃ was used as the hole scavenger in an aqueous system with ZnS.¹³⁴ The study demonstrated that KHCO₃ acted as an effective hole scavenger as well as a buffer to mitigate the pH change induced by the CO₂ saturation. This phenomenon, however, was not observed when only K₂SO₃ was used as the hole scavenging agent.

The optimised solution with 0.1 g of colloidal ZnS, 0.1 M K₂SO₃ and 0.5 M KHCO₃ achieved 464.2 and 81.3 μmol of HCOOH and CO, respectively, under UV-vis irradiation (Table 2 entry 2).¹³⁴ The selectivity towards HCOOH was reported to be 12.5%, and this could be improved to 95.0% when Cd was added to the colloidal ZnS suspension as the co-catalyst.

Inorganic salts (*e.g.*, NaOH, Na₂S, *etc.*) have been reported to have a significant effect on CO₂PR.^{97,132,134,135} The addition of NaOH had been shown to increase the solubility of CO₂ compared to pure H₂O because the OH⁻ ions provided by NaOH in aqueous solution reacted with the dissolved CO₂, and transformed into CO₃²⁻ and further into HCO₃⁻ in the CO₂ saturated system.¹³⁶ It was suggested that the high



Table 2 Photocatalytic CO₂ reduction yields obtained by various photocatalyst after adding hole scavenger(s)

No.	Photocatalyst	Hole scavenger	Function/role	Product(s) of CO ₂ photoreduction (μmol g _{catalyst} ⁻¹ h ⁻¹)	Ref.
Inorganic					
1.	ZnS quantum crystallites	0.70 M NaH ₂ PO ₂ 0.48 M Na ₂ S	Electron donor Sulphur vacancy suppressor	HCOOH 75.10 CO 1.70	132
2.	ZnS	0.1 M K ₂ SO ₃ 0.1 M K ₂ SO ₃ ⁺ 0.5 M KHCO ₃	Hole scavenger Electron donor Buffer solution	HCOOH ~250.00 HCOOH 580.30	134
3.	Zn-doped Ga ₂ O ₃	0.1 M NaHCO ₃	Hole scavenger	CO 117.00	138
4.	Ag-loaded SrNb ₂ O ₆	0.1 M NaHCO ₃	CO ₂ supply	CO ~4.00	71
5.	Ag-loaded Sr ₂ Nb ₂ O ₇			CO ~38.40	
6.	Sr and Ag co-loaded NaTaO ₃	0.1 M NaHCO ₃	Buffer for supplying CO ₂	CO ~352.00	94
7.	Ni-Al layered double hydroxides (LDHs)	0.1 M NaCl	Hole scavenger	CO 112.80	139
8.	BiVO ₄	1.0 M NaOH	Hole scavenger	CH ₃ OH 5.52	97
Organic					
9.	CdS	Acetonitrile + dichloromethane 1.0 mol dm ⁻³ 2-propanol	Surface modifier Surface modifier Hole scavenger	(CH ₃) ₂ CO ~0.24 μmol with 70 μM of CdS powder (CH ₃) ₂ CO ~0.19 μmol with 70 μM of CdS powder	140
10.	Wurtzite-ZnS	Isopropanol Ethylene glycol	Hole scavenger Hole scavenger	HCOOH ~40 ppm g _{catalyst} ⁻¹ h ⁻¹ HCOOH ~90 ppm g _{catalyst} ⁻¹ h ⁻¹	141
11.	Mononuclear Ru complex/C ₃ N ₄	4 : 1 of <i>N,N</i> -dimethylacetamide (DMA) : triethanolamine (TEOA)	Proton quencher Electron donor	HCOOH ~1100.00	142
12.	Bi-nuclear Ru complex/Ag-loaded C ₃ N ₄	4 : 1 of <i>N,N</i> -dimethylacetamide (DMA) : triethanolamine (TEOA)	Proton quencher Electron donor	HCOOH ~2115.00	143
13.	Bi-nuclear Ru complex/Ag-loaded C ₃ N ₄	1.0 mM ethylenediaminetetraacetic acid disodium salt dihydrate, EDTA·Na ₂	Electron donor	HCOOH ~31.67	144
14.		1.0 mM ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA·Na ₂) + 0.1 M K ₂ CO ₃	Electron donor Surface modifier	HCOOH ~83.33	

concentration of HCO₃⁻ present in the system could accelerate the photoreduction reaction, thereby enhancing the photoreduction performance.^{136,137} The direct consumption of HCO₃²⁻ to produce CO was observed in a CO₂ aqueous solution using a Zn-doped Ga₂O₃ photocatalyst.¹³⁸ This observation was further investigated by Nakanishi *et al.*, in which the production of CO occurred after transforming HCO₃⁻ into CO₂.⁹⁴ Therefore, the addition of HCO₃⁻ increased the CO₂ supply in the aqueous system, but did not enhance the numbers of reacted electrons and holes. In other words, under basic conditions, H₂ production could be significantly suppressed, resulting in a high selectivity of CO from CO₂. Jin *et al.* concurred that the addition of NaOH promoted the formation of HCO₃⁻; however, the production of methanol was observed in the photocatalytic system with a BiVO₄ photocatalyst.⁹⁷

The addition of NaOH, Na₂CO₃ and NaHCO₃ to the CO₂ photoreduction aqueous solution was shown to promote the photoproduction of CO, whereas H₂SO₄ and NaCl were found to favour water splitting, leading to the production of H₂.^{90,94,136,137} However, a recent study has proposed that the inclusion of Cl⁻ from NaCl could scavenge the photogenerated holes for the CO₂ photocatalytic reduction process in a aqueous solution over Ni-

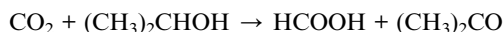
Al layered double hydroxides.¹³⁹ The selectivity towards CO over H₂ was 86% when NaCl was added into the photoreduction system (~6.95 and ~1.16 μmol g⁻¹ h⁻¹ of CO and H₂, respectively), whereas in the absence of a scavenging agent, the selectivity towards CO over H₂ was only 54% (~3.15 and ~2.63 μmol g⁻¹ h⁻¹ of CO and H₂, respectively). The authors also pointed out that the addition of NaHCO₃ and Na₂CO₃ promoted the production of H₂ *via* the reduction of H⁺ derived from H₂O instead of the CO₂PR. Neither Na₂SO₄ nor NaNO₃ could positively enhance the production of CO. A similar extent of CO evolution and selectivity were also observed when other chloride salts were added, namely CsCl (~8 μmol g⁻¹ h⁻¹ of CO, 82%), MgCl₂ (~7 μmol g⁻¹ h⁻¹ of CO, 82%) and CaCl₂ (~7.5 μmol g⁻¹ h⁻¹ of CO, 82%). However, other halogenide salts (NaBr and NaI) showed a weaker photoreduction ability than NaCl.

3.2 Organic hole scavengers

Since the last century, ZnS had been used as photocatalyst for the CO₂PR.^{146,147} Triethylamine (TEA) showed its feasibility to be used as the hole scavenger, inhibiting the photocorrosion for sulphite photocatalysts.⁷ In ZnS systems, 2-propanol was one of



the common hole scavengers for CO₂PR. A previous report proposed that the light energy could be stored within the light-induced reaction given as



The Gibbs free energy of this reaction is +62.8 kJ mol⁻¹ at 25 °C.¹⁴⁷

In a system of Cd-loaded ZnS, CO₂ photoproducted formic acid with a quantum efficiency 32.5% in the presence of 1 M 2-propanol.¹⁴⁷ Further increasing the Cd concentration resulted in the formation of CO. A study revealed that CdS was capable of photoreducing CO₂ to CO when *N,N*-dimethylformamide (DMF) containing 1 v/v% water was employed in the system.¹⁴⁸ A similar observation was reported, in which CO was photoproducted when CdS was dispersed in DMF under the irradiation of a 500 W mercury lamp with a 300 nm cut off filter.¹⁴⁰ When DMF was substituted with a low polarity solvent, such as CCl₄ and CH₂Cl₂, CO production was dominant, whereas when using a high polar solvent, such as H₂O, formate was produced. This was because the adsorbability of the CO₂^{•-}, an intermediate species after the activation of CO₂, was strongly dependent on the polarity of the solvent used. For instance, low polarity molecules enabled strong adsorption of CO₂^{•-} on the Cd sites of CdS through the carbon atom of CO₂^{•-}, which was not highly solvated in solvents of low polarity, resulting in the formation of CO. When high polar solvents were used, CO₂^{•-} was stabilised in the system and established only weak interactions with the photocatalyst. As a result, CO₂^{•-} tended to react with a proton and produced formate.

A recent study suggested that the CO₂ photoreduction process can be greener when glycerol, which is a green solvent derived from vegetable oil, was used as the hole scavenger instead of petroleum-derived solvents.¹⁴¹ In this study, wurtzite ZnS facilitated the photoproduction of formic acid from CO₂ with an apparent quantum efficiency of 3.2% and 0.9% when glycerol and 2-propanol, respectively, were employed as the hole scavenger.

Cyclohexanol was used as the hole scavenger for the CO₂ photoreduction under UV light irradiation.¹⁴⁹ The optimised sample exhibited the production of cyclohexyl formate and cyclohexanone (178.1 and 170.2 μmol g_{catalyst}⁻¹, respectively) after 8 h. The authors elucidated that the production of cyclohexanone was slightly lower than that of cyclohexyl formate because some of the photogenerated holes were consumed by cyclohexanol to form cyclohexyl ether.

A recent study demonstrated that a Ru(II)-complex/C₃N₄ nanocomposite could induce the photocatalytic CO₂ reduction by using a mixture of solvents (*N,N*-dimethylacetamide and DMA/TEOA).¹⁴² The apparent quantum efficiency achieved was 5.7% at 400 nm (Table 2 Entry 12). In addition, the product selectivity of the Ru(II)-complex/C₃N₄ nanocomposite could be enhanced through manipulating the solvent used (Fig. 13).¹⁴⁵

In order to avoid using organic solvents as the medium, the mononuclear Ru(II) complex proposed in a previous study¹⁴² was replaced with a binuclear Ru(II) complex coupled with Ag/C₃N₄

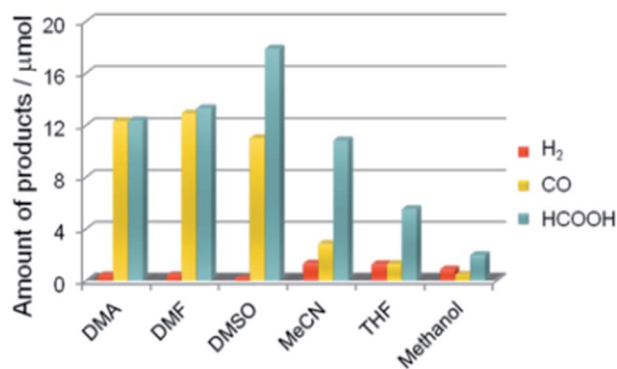


Fig. 13 Product distribution of visible light ($\lambda > 400$ nm) CO₂ reduction using Ru(II) complex/C₃N₄ as a photocatalyst and various solvents under a CO₂ atmosphere (DMSO: dimethyl sulfoxide, MeCN: acetonitrile, and THF: tetrahydrofuran). Reproduced from ref. 145 with permission.

and was employed as the photocatalyst (Table 2 entry 13).¹⁴³ Since no reduction product was obtained in pure water, a hole scavenger (ethylenediaminetetraacetic acid disodium salt dihydrate, EDTA·Na₂) was added to promote the photocatalytic CO₂ reduction in water. The main product was HCOOH, and H₂ was produced as a by-product under visible light irradiation ($\lambda > 400$ nm). Other hole scavenging agents (e.g., potassium oxalate and sodium ascorbate) were shown to be useful for the CO₂PR. Among the three hole scavenging agents, sodium ascorbate exhibited the best performance with 31.7 μmol and 86% selectivity towards HCOOH. The HCOOH production could be further enhanced to 83.3 μmol with selectivity 97% when K₂CO₃ (0.1 M) was used as an additive.¹⁴⁴ However, the production of H₂ was reduced by half.

The introduction of organic and inorganic hole scavenging agents has exhibited advantages to enhance the efficiency of CO₂PR. The presence of hole scavenging agents in the CO₂PR process is necessary if the oxidation reaction in the CO₂PR cannot be inhibited by the photocatalyst. Moreover, to avoid carbon contamination and false positive errors for the photogeneration of hydrocarbons in the CO₂PR process, inorganic hole scavenging agents are preferred.

4. Conclusions and future directions

To date, significant achievements have been made in the design and fabrication of photocatalysts and the optimisation of photocatalytic systems. CO₂PR using metal sulphides, oxides, oxynitrides and nitrides accumulated so far have offered alternative photocatalytic materials other than TiO₂. Material properties, including the surface area, light harvesting, and charge generation, separation and transportation, have been manipulated through the structural and morphological control during the fabrication processes, leading to enhanced CO₂PR performance. Amongst the non-titania photocatalysts (metal sulphides, oxides, oxynitrides and nitrides) reviewed here, the ultrathin W₁₈O₄₉ exhibited the highest CH₄ yield (2200 μmol g_{catalyst}⁻¹ h⁻¹) from CO₂ under visible light irradiation. The



presence of oxygen vacancies was suggested to play an important role in the CO₂PR. On the other hand, the addition of inorganic salts or organic solvents into an aqueous system has shown to effectively scavenge the photogenerated holes and/or increase CO₂ solubility.

Although significant studies have been carried out on CO₂PR, some challenges still remain. Firstly, an in-depth understanding of the working mechanism in a CO₂ photoreduction process is still not well understood. Hence, a trial-and-error approach was used when fabricating photocatalysts, attempting to achieve a high CO₂PR efficiency. Secondly, the insight into the CO₂PR in the presence of hole scavenging agent(s) is not available. Moreover, due to this lack of knowledge, a rational design to combine state-of-art of photocatalysts with the desired hole scavenging agent(s) for carbon fuel production is difficult to achieve. Therefore, while more effort is required in material advancement, studies of the combined effect of the proposed photocatalyst with a hole scavenger should be encouraged. In addition, further investigation of CO₂PR at the molecular level through *in situ* characterisation techniques should be carried out as this is key to boosting the efficiency of CO₂PR.

Conflicts of interest

There are no conflicts to declare.

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