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1 **Photocatalysts for CO₂ Reduction and Computational Insight**

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26 **Abstract**

27 Global warming is caused by excessive CO₂ production, and reducing CO₂ emissions is
28 a viable way to counteract this. It has been extensively studied how light-driven
29 processes, particularly photocatalytic systems, can transform solar energy into chemical
30 energy. In the present review exercise, the mechanism of CO₂ reduction is described
31 using calculations based on density functional theory (DFT), and comparisons are also
32 made with regard to typical light-driven devices. Additionally, the traits of potential

33 materials—including metal-organic frameworks (MOFs), metal complexes,
34 semiconductors, Z-scheme (metal complexes/semiconductors, two semiconductors,
35 Dye-sensitized semiconductors) and organic semiconductors etc.—are described in
36 depth to show how these traits affect the CO₂ adsorption, activation, and desorption
37 processes. Also summarized are a number of methods for enhancing the selectivity and
38 efficiency of catalytic reactions. Lastly, the challenges and future outlook of light-
39 driven reactions for CO₂ reduction are presented.

40 **Keywords:** Photocatalysts; CO₂ reduction; Semiconductors; Z-schemes; MOFs

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57 **1. Introduction**

58 The global increase in population has a correspondingly warranted an increase in the
59 usage of fossil fuels for the existence of mankind. This is a result of the need to use
60 some technologies powered and/or driven via the use of various forms of fossil fuels,
61 with associated emission of CO₂ into the atmosphere at a yearly estimated emission rate
62 of 3.0×10^{13} kg per year [1]. Simply put, this large use of fossil fuels has only been able
63 to satisfy the world energy demand by ~81% [2]. The temperature rises due to this huge
64 CO₂ input into the atmosphere causing a number of harms to the global populace such

65 as global warming, flooding, etc. This was corroborated at the Paris Conference held by
66 the United Nations Agreement, which highlighted that the combustion of fossil fuels,
67 leading to the emission of CO₂ and stored in the atmosphere, could increase the global
68 temperature of the atmosphere owing to the unequal intensity of incoming and outgoing
69 solar energy [3]. Hence, in order to ameliorate the various health and environmental
70 impacts, due to CO₂ emission, various reduction and/or transformation technologies
71 have been designed by researchers.

72 Amongst the available technologies that have been applied to convert or reduce CO₂
73 are photocatalytic transformation [4,5], thermal conversion, electrocatalytic conversion
74 [6,7], biological approach (fixation) [8,9], electrochemical transformation [10,11] and
75 so on. In terms of efficiency, the application of catalytic or thermal transformation is
76 limited due to the involvement of high pressure and temperature with associated or
77 elevated process operational cost; although the two technologies have been found to be
78 effective [12,13]. The efficiency of the electrochemical conversion of CO₂ to value-
79 added hydrocarbon fuels is low and limits its widest application [14]. Likewise, the
80 biological approach is impractical because of the requirements of enzyme production
81 and the need for regeneration that are germane to the functionality of the process
82 [15,16]. However, photocatalytic conversion has overwhelming merits when compared
83 to others, as it primarily makes use of solar energy and photocatalyst for conversion.

84 Photocatalytic conversion has been described as an “artificial photosynthetic” route for
85 the transformation of CO₂ to useful hydrocarbon and hydrogen fuels. In this vein,
86 various previous studies have reported the use of a photocatalytic approach for the
87 reduction and/or conversion of CO₂ [17] to methanoic acid (HCOOH) [18,19], methane
88 (CH₄) [20,21], methanal (HCHO) [22] carbon monoxide (CO) and [23,24] and
89 methanol (CH₃OH) [7,25]. Sequel to the applicability, effectiveness, eco-friendliness,
90 cheapness and practicability of this method, several authors have worked on and/or
91 reported the use of different photocatalysts to capture and reduce, by conversion of
92 CO₂, to the above-mentioned products via “artificial photosynthetic” route. For
93 instance, several researchers have worked on the use of metal-organic frameworks,
94 organics, z-scheme, semiconductors, and metal complexes as photocatalysts for CO₂
95 conversion. In addition, a number of studies have been done in the use of computational
96 studies to investigate the effectiveness or efficacy of photocatalysts for CO₂ conversion

97 in the presence of solar energy, before experimental work is done. Examples are the use
98 of Density Functional Theory (DFT) and Artificial Intelligence (AI) tools such as
99 Machine Learning (ML) and Deep Learning (DL). These tools are and becoming
100 widely used and might be integrated into the conventional workflow research workflow
101 of photocatalytic conversion of CO₂ conversion.

102 Recently, Sharma et al. published a review article on photocatalytic conversion or
103 reduction of CO₂ using ZnO/carbon hybrid [26]. Wang et al. evaluated research papers
104 published on CO₂ reduction using copper-based photocatalysts [27]. Devi et al.
105 presented previous reports, by evaluation, on photoelectrochemical, electrochemical
106 and photocatalytic reduction of CO₂ [28]. This article either narrow their evaluation to a
107 single material as photocatalyst, or compare a limited number of methods. However, in
108 this review, we reported on the usefulness, effectiveness and applicability of the
109 computational approach in photo-catalytically reducing and/or transforming CO₂ as
110 described in section 2 of this article. We explained briefly the fundamental mechanism
111 of photocatalysis in section 3. Furthermore, detailed formation gathered from scattered
112 literatures on metal complexes, metal oxides, z-scheme, S-scheme and organic as
113 enviable photocatalysts were thoroughly evaluated and presented in sections 4, 5, 7, 8,
114 and 9 respectively. Metal-organic frameworks (MOFs), which are porous materials for
115 adsorption, and which also possess photocatalytic properties [29], were discussed in
116 section 6, by evaluating their CO₂ capture capacity, CO₂ photoconversion, mechanism
117 of CO₂ photo-reduction and the challenges of MOFs synthesis and application. Finally,
118 the review concludes by advocating the use of theoretical (computational) studies in the
119 conduction of experiments for photocatalytic CO₂ reduction or conversion, in order to
120 have a prior understanding of the effectiveness of photocatalysts to be employed for the
121 transformation process.

122 **2. Computational studies of photocatalysts for CO₂ reduction**

123 Computational studies have become quite popular in most recent studies involving the
124 application of materials that have photosensitizing properties for CO₂ reduction [1–4],
125 particularly the Density Functional Theory (DFT) method making it an indispensable
126 tool in present-day research. This is no surprise as DFT studies complement
127 experimental works by providing atomistic insights into how the molecules studied
128 have photosensitizing abilities capable of reducing CO₂. DFT studies help to understand
129 the mechanism of action or pathway of CO₂ reduction by the studied materials. This

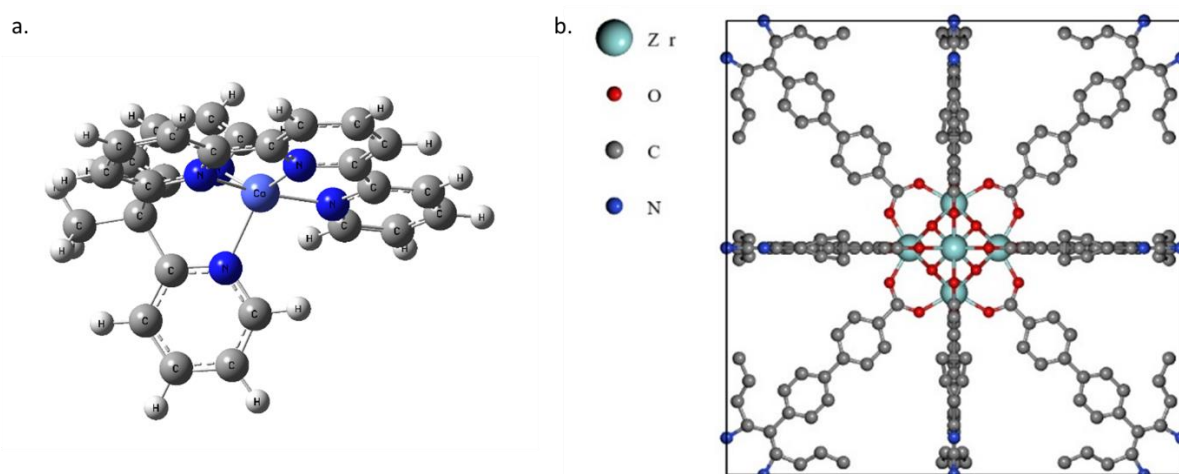
130 aids the modification and development of better materials. DFT has many tools
131 including Geometry optimization, electrostatic potential maps, TD-DFT (Time-
132 Dependent Density Functional Theory) for UV-Visible calculated spectra, molecular
133 orbital maps, and intrinsic reaction coordinate systems, free energy profiles which are
134 used in studying these materials. However, these are often used for studying molecules.
135 On the other hand, Periodic DFT can study larger systems which include the molecules
136 on catalytic surfaces.

137 Geometry optimization is usually the first calculation carried out on the studied system.
138 In the case where the studied material is made up of complexes that contain transition
139 metals. This can be sometimes challenging as a trade-off is often made between
140 accuracy and computational costs this is further exacerbated by the spin-state energetics
141 [5–8]. The B3LYP functional [9] with the 6-31G(d,p) basis sets is a renowned and
142 accurate level of theory and basis set respectively for non-metal atoms in the system
143 whilst the TZVP (Triple Zeta Valence with Polarization) basis set is more reliable for
144 metals even though it comes at an additional computational cost [10,11]. Geometry
145 optimizations are often used to compare and validate the bond parameters (bond lengths
146 and angle) to experimental crystal structures derived from Single-crystal X-ray
147 diffraction. The molecular orbitals consist of the HOMO (Highest Occupied Molecular
148 Orbital) and Lowest Unoccupied Molecular Orbital (LUMO) and are also used in
149 calculating energy gaps and deducing the wavelength of the excitation energies of the
150 studied material.

151 For instance, in the DFT calculations done by Zhou et al [12] on MCOF-Ti₆Cu₃, a
152 metallic cluster catalyst deduced from the closeness of the HOMO and LUMO the
153 cluster could be excited by infrared light (1704.16 nm) excitation energy. The HOMO-
154 LUMO maps also help to understand the distribution of electron clouds within the
155 studied material and the transfer of electrons during the excitation process. This can be
156 quite useful in confirming what was observed from in situ X-ray photoelectron
157 spectroscopy (XPS) experimental measurements. Zhou et al were able to prove with the
158 aid of DFT that reduction occurred on the Cu cluster whilst oxidation occurred on the
159 Ti cluster. DFT studies are also used to investigate the non-covalent interactions (NCI)
160 in the metallization of porphyrinic photosensitizers. Yin et al [13] employed DFT to
161 investigate the NCI between porphyrin-based hydrogen-bonded organic framework
162 molecules and different metals (Co, Ni, Cu, Zn). Their result showed that upon

163 metallization of the porphyrinic material the core changes the π - π stacking interaction
164 and consequently the NCI between interlayer adjacent porphyrin rings. This was further
165 confirmed by the orbital overlaps when observing the HOMO-LUMO maps.
166 Summarily, this showed that metallization bestowed the porphyrins with different
167 catalytic activities useful for CO₂ photoreduction. Amongst the porphyrin-metallization
168 studied, the one with cobalt showed optimal performance. However, the recent work by
169 Torre et al [14] used DFT calculations to predict that the source of different behaviour
170 observed in Fe²⁺ and Co²⁺ complexes is the electronic configuration of the reduced
171 species. That is from Co²⁺ to Co⁺, the reduction is predicted to be metal-centred leading
172 to an observed loss in CO₂ reduction reaction (CO₂RR) activity and increased
173 Hydrogen Evolution Reaction (HER) from a formal Co⁺ than Co²⁺. Further reduction
174 from Co⁺ to Co⁰ is accompanied by significant electron rearrangement to a metal-ligand
175 coupling interaction in the form of an open shell doublet with a formal Co²⁺ center
176 bound to a twice reduced ligand, in this case (tpyPY2Me^{**})². Though experimental
177 analysis such as electrolysis and photocatalysis experiments suggest that this reduced
178 specie is capable of reducing CO₂ to CO but not stable which leads to the formation of
179 a nanoparticle film. When used in metal-ligand exchange coupling, the understanding
180 of this instability caused by the open-shell doublet is due to DFT calculations. **Figure 1**
181 shows the DFT optimized structure of the cobalt metal-ligand.

182



183

184 **Figure 1.** (a) DFT optimized structure of Co⁺ from calculations using ω B97X-D
185 functionals and CH₃CN solvent adapted from coordinates in [14] and (b) unit cell of
186 TNP-MOF adapted from CDCC structure in [15]

187 Also, DFT particularly Time-Dependent Density Functional Theory (TD-DFT) has
188 been used to understand the light absorption properties of Tetrakis (4-carboxbiphenyl)
189 naphthoporphyrin linker in metal organic frameworks (TNP-MOF) used in
190 photosensitive CO₂RR [16]. The unit cell of TNP-MOF is illustrated in **Figure 1**. The
191 TDDFT calculated absorption spectrum showed that the Q-band of TNP was much
192 higher than other ligands studied and which was in agreement with what was observed
193 experimentally from steady-state absorption spectra using Ultraviolet photoelectron
194 spectroscopy. Ditto applied to the gaps between HOMO and LUMO orbitals which was
195 in concordance with the change trend observed in band positions experimentally. A
196 linear proportional relationship was observed between the extension of π -conjugated
197 system of the linker and the delocalization of the π conjugated electron leading to a red
198 shift in absorption of the linkers. The theoretical results suggested that the energy levels
199 of the linkers studied in this work [16] were feasible for the reduction of CO₂ into
200 HCOOH.

201 Another relatively new computational method besides DFT that is applied in
202 photosensitive CO₂ reduction is the application of Artificial Intelligence (AI) tools such
203 as Machine Learning (ML) and Deep Learning (DL). In a recent work, Li et al [17]
204 applied an ML classification algorithm to predict catalytic performance of MOFs on a
205 dataset derived from about 100 published experimental papers. This work discovered
206 that the following metals -Mn, V, Cu, Ni, Zr and Y alongside these ligands (tactmb,
207 tdcbbp, TCPP and H₃L) could be combined to make 24 MOFs which are potential
208 catalyst for CO₂ reduction. This work tested and compared five ML algorithms-
209 Support Vector Classifier (SVC), K-Nearest Neighbor (KNN), Decision Trees (DT),
210 Stochastic Gradient Descent (SGD) and Neural Network (NN) on 1311 hypothetical
211 MOFs. The SVC and NN had the best metric scores with respect to performance from
212 their F1- score and accuracy. The implementation of AI would help facilitate the
213 discovery of new photosensitive materials capable of CO₂ reduction. However, it is
214 important to note that computational techniques serve a complementary purpose to aid
215 experimental work in material discovery.

216 **3. Fundamental mechanism of the photocatalysis**

217 Photocatalysis is considered to be an artificial form of photosynthesis whereby solar
218 energy is harvested for the conversion of CO₂. The pioneer work regarding
219 photocatalysis was reported by Halman and his group using p-GaAs as photo-

220 electrocatalyst over a cathodic bias [18]. The reduction of CO₂ by photocatalysis is
 221 similar in mechanism to the natural photosynthesis, which can be explained using three
 222 separate but linked steps: (i) the absorption of solar energy (ii) the separation of charges
 223 and (iii) surface redox reaction [19]. The light absorption induces light excited ‘photo-
 224 hole and photo-electron’ formation in a light harvesting material (semiconductors) [20].
 225 First, a light energy of equal or greater energy is supplied to promote electron(s) from
 226 the photocatalyst valence band (VB) to its conduction band (CB) to produce photo-hole
 227 (h^+) and photo-electron (e^-), respectively and the effectiveness of the semiconductor
 228 depended on its design in terms of band gap energy [21]. The second stage are,
 229 however, characterized with different processes, like transfer of photogenerated charges
 230 to the surface, in-band transitions, electron-hole recombination and others [22]. The last
 231 stage describes the participation of the surface charges in redox reaction, whereby the
 232 photo-electrons in the CB induces the reduction of CO₂ to various products. Also,
 233 before reduction of CO₂ takes place, the mechanism of reduction entails the
 234 coordination of the molecule (CO₂) to photocatalyst metal center for activation and
 235 metal adduct formation and then followed by the transferring of proton to metal adducts
 236 intermediates to form different products, depending on the nature of photocatalyst used
 237 [23].

238 Thermodynamically, due to shorter period of relaxation of electron-hole, it is less likely
 239 to have equilibrium between the forbidden bands (energy difference between the
 240 bottom of CB and top of VB) than an internal equilibrium existing within the energy
 241 levels [24]. Representing the electronic states in equilibrium (quasi-equilibrium states)
 242 as given in equations 1, 2 and 3, it is possible deduce the thermodynamic feasibility of
 243 redox reaction on catalyst surface [25]:

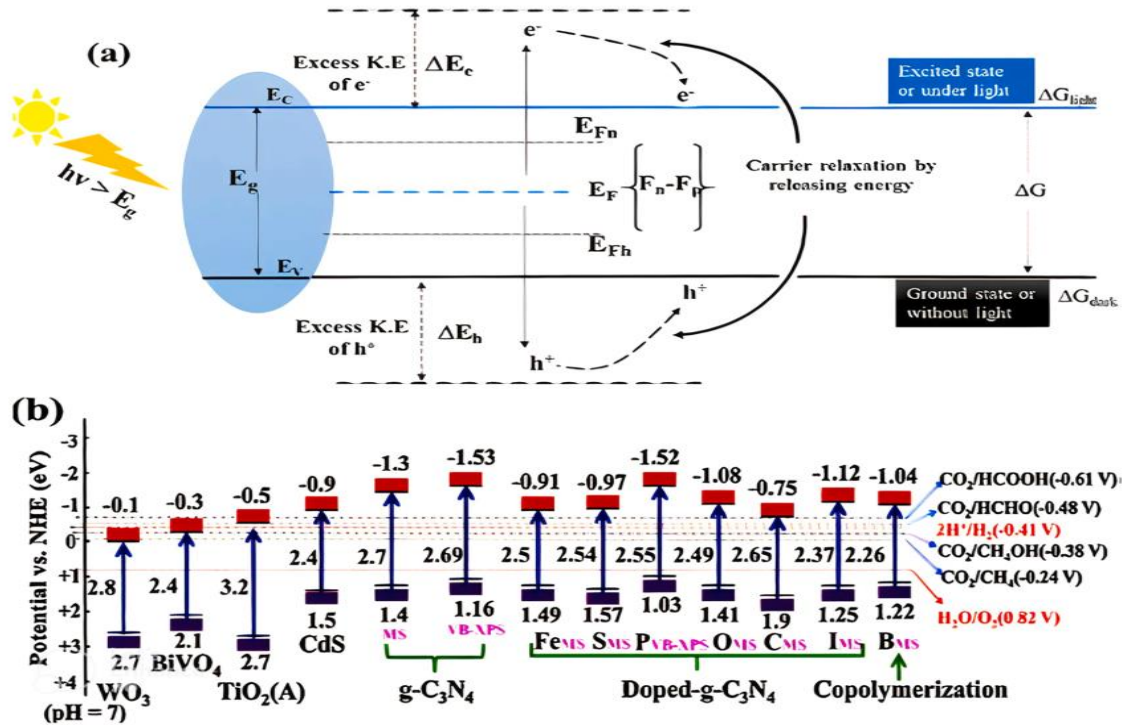
$$244 \quad F_n = CB + KT \ln \frac{n}{N_c} \text{-----} 1$$

$$245 \quad F_p = VB + KT \ln \frac{p}{N_v} \text{-----} 2$$

$$246 \quad \Delta G = -|F_n - F_p| = -E_g - KT \ln \frac{pn}{N_c N_v} \text{-----} 3$$

247 VB and CB have their usual meanings while N_v and N_c means effective density of
 248 states for VB and CB, respectively. K , p , and n represents Boltzmann constant, hole
 249 and electron concentrations, respectively. Inferentially, according to equation 3, when

250 the difference between pseudo-fermi levels, ΔG becomes more negative and the
 251 photocatalytic redox reaction is more spontaneous. Furthermore, the position of CB
 252 dictates CO₂ reduction thermodynamics. **Figure 2** reveals an overview of the tendency
 253 as well as the standard potentials of different types of semiconductors for production of
 254 value-added-products from CO₂ reduction.



255 **Figure 2:** ΔG and semiconductor thermodynamics with and without illumination (a);
 256 semiconductor band potential and their applicability for forming value-added-products
 257 (b). Adapted with permission from [26]. Copyright (2018) Elsevier

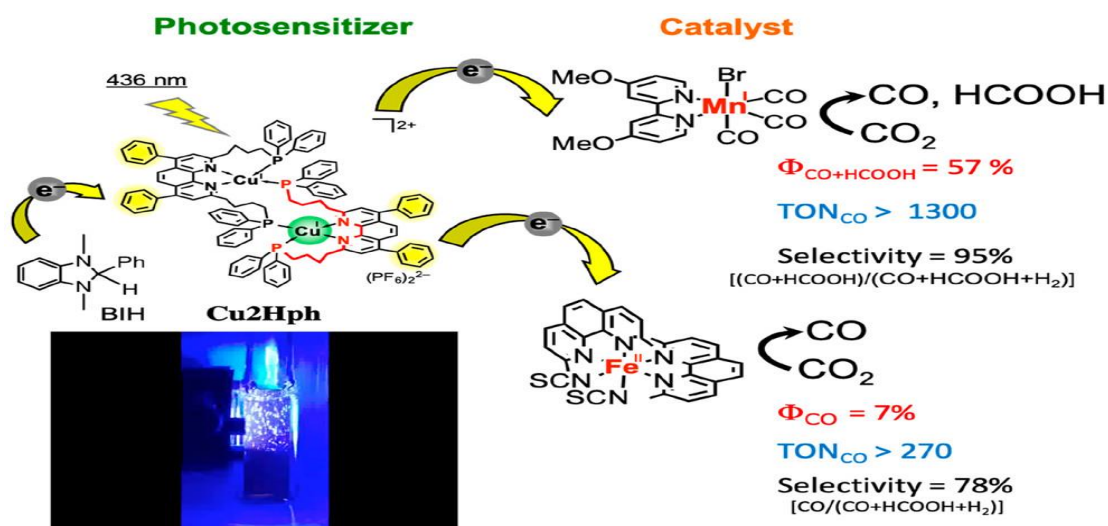
259 4. Metal-complex photocatalysts

260 Experimentally, the application of metal-complex photocatalysts has attracted attention
 261 and research in abating CO₂ and findings revealed that it is possible to precisely control
 262 the functionality of metal complexes, including their photophysical, electrochemical,
 263 and catalytic properties, by designing them at the molecular level [27]. As such, the
 264 photocatalytic activity of metal complexes for CO₂ reduction into hydrocarbon fuels
 265 has been explored and reported in various previous studies. For example, Hawecker and
 266 colleagues[28] for instance, used [fac-Re(bpy) (CO)₃Cl] (bpy = 2,2'-bipyridine) to
 267 demonstrate one of the first metal complexes as an effective homogeneous catalyst for
 268 selective and sustained photochemical reduction of CO₂ to CO in 1986. The researchers

269 measured a quantum yield of 14% and a faradic efficiency of 98% in the presence of
270 additional Cl⁻ ions. Photocatalytic CO₂ reduction using metal complexes has evolved
271 since then, and new viewpoints have fundamentally transformed the field of study.

272 It is important to mention that a photosensitizer and a CO₂-reduction catalyst are the
273 two main components of the bulk of contemporary metal-complex-based homogeneous
274 photocatalytic systems. As an illustration, Kumagai and his colleagues [29] recently
275 developed a mixed system of a ring-shaped Re(I) trinuclear complex as a
276 photosensitizer and fac-[Re(bpy)(CO)₃{OC₂H₄N(C₂H₄OH)₂}] as a catalyst which
277 selectively photocatalyzed CO₂ reduction to CO with the highest quantum yield of 82%
278 and a turnover number (TON) of over 600. The group also investigated a Cu(I)
279 dinuclear complex as a photosensitizer and fac-Mn(bpy)(CO)₃Br or Fe(phen)₂(SCN)₂
280 as catalysts (**Figure 3**). The total quantum yield of CO and HCOOH from CO₂ was
281 57% with TON_{CO + HCOOH} >1300 against fac-Mn(bpy)(CO)₃Br] and the quantum yield
282 of CO recorded against Fe(phen)₂(SCN)₂ was 7% with TON_{CO} >270. In another
283 example, Takeda and co-workers [30] designed CO₂ reduction photocatalysts
284 employing [Cu₂(P₂bph)₂]²⁺ (CuPS) (P₂bph = 4,7-diphenyl-2,9-
285 di(diphenylphosphinotetramethylene)-1,10-phenanthroline) as a redox photosensitizer
286 and fac-Mn(X₂bpy)(CO)₃Br (Mn(4X)) (X₂bpy = 4,4'-X₂-2,2'-bipyridine (X = -H and
287 -OMe) or Mn(6mes) (6mes = 6,6'-(mesityl)2-2,2'-bipyridine)) as the catalyst. The CO₂
288 reduction process was 95% selective, the overall quantum yield of CO₂ reduction
289 products was 57%, and the Mn catalyst had a TON >1300.

290 However, because such transfer necessitates physical contact between the
291 photosensitizer and the catalyst, electron transfer from the one-electron-reduced species
292 to the catalyst is frequently the rate-determining step in two-component homogeneous
293 systems like these. Despite the fact that these metal complexes demonstrated
294 impressive photocatalytic activity for CO₂ reduction, studies have revealed that metal
295 complexes suffer a setback when it comes to inducing a continuous selective reaction in
296 a mixture of reactants and products due to the different reaction conditions required for
297 CO₂ reduction.



298

299 **Figure 3.** Mechanism of photocatalytic reduction of CO₂ by Cu₂Hph as photosensitizer
 300 and fac-Mn(MeO-bpy)(CO)₃Br or Fe(phen)₂(SCN)₂ as catalysts. Adapted with
 301 permission from [29]. Copyright (2022) American Chemical Society

302 5. Metal Oxide Photocatalysts

303 Fujishima and Honda [31] first demonstrated the use of metal oxides as a photocatalyst
 304 for CO₂ reduction in the 1970s, using a rutile-TiO₂-based photoelectrochemical cell for
 305 water splitting. Since then, several studies have been published that use various
 306 approaches to improve the photocatalytic performance of semiconductors for CO₂
 307 reduction, such as the addition of cocatalysts or other surface modifications. From the
 308 available studies, semiconductors offer superior photo-oxidation activity, stability and
 309 recyclability [32]. One conspicuous advantage of semiconductor photocatalysts
 310 compared to its counterpart (metal complex) is that it can use water as an electron
 311 donor under the conditions employed for photocatalytic reduction of CO₂ [33].
 312 However, the reduction of CO₂ in an aqueous solution is limited by low quantum
 313 efficiency due to preferential H₂ production under visible light.

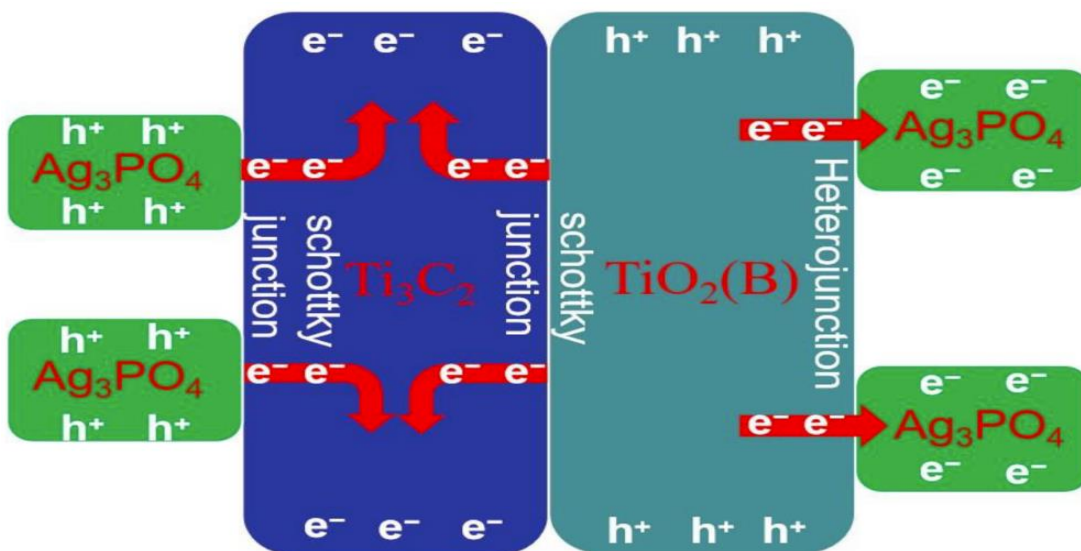
314 Several metal oxide semiconductors have been employed in the recent decade to reduce
 315 CO₂ emissions by employing water as an electron donor [34,35]. The huge band gap,
 316 however, prevents it from using visible or solar radiation. For instance, Guo and co-
 317 workers [36] demonstrated photoreduction capability of AgTaO₃ for CO₂ reduction
 318 utilizing H₂O as an electron source. AgTaO₃ with Ag cocatalyst loaded by photo
 319 deposition demonstrated the maximum activity for CO generation among those with Pt,
 320 Rh, or Cu cocatalysts after adjusting the synthetic conditions and performing different

321 surface modification with variety of cocatalysts. When core/shell structured metal
322 nanoparticles were combined with Cr_2O_3 , AgTaO_3 photocatalyst demonstrated CH_4
323 evolution activity in photocatalytic CO_2 conversion, indicating that Cr_2O_3 species
324 accelerated the hydrogenation process of CO_2 reduction. The results of this study
325 showed that cocatalyst decoration changed conversion products and was crucial for
326 multielectron photoreduction of CO_2 . In another study, Liu and co-researchers
327 [37] presented a way for improving the solar fuel generation rate of TiO_2 by loading
328 cocatalysts, specifically bimetallic Cu-Pt and CuO, through two-step photodeposition
329 procedures. The photocatalytic H_2 generation rate of the Cu-Pt/ TiO_2 -CuO sample under
330 simulated sunlight conditions is $173.7 \mu\text{mol/g.h}$. For photocatalytic CO_2 reduction by
331 water, the Cu-Pt/ TiO_2 -CuO sample displays the release of H_2 , O_2 , CO , CH_4 , and
332 CH_3OH , with CO being the predominant reaction product. The O_2 and CO yields for
333 LED-405 and LED-425 are typically 4.2 and 6.2 and 2.1 and $3.2 \mu\text{mol/h.g}$,
334 respectively; the CO_2 -to- CO conversion ratios for separated carriers are 73.8 and
335 76.19%.

336 MXene materials have recently been discovered to be ideal co-catalysts and/or catalyst
337 supports for improving semiconductor performance for photocatalytic CO_2 reduction.
338 According to a recent review work carried out by Shen and co-workers [38], the
339 inclusion of M-Xene as catalyst support has been discovered to improve the separation
340 of electrons and positive holes, improve the light absorption and photochemical effect,
341 enhancing the adsorption and activation of CO_2 and inhibition of photo-corrosion. In
342 one of the earlier computational studies of MXene as a potential catalyst/cocatalyst for
343 CO_2 reduction, Zhang et al. [39] used first-principles simulations to examine CO_2
344 catalytic reduction processes at oxygen vacancies in three MXene (Ti_2CO_2 , V_2CO_2 and
345 $\text{Ti}_3\text{C}_2\text{O}_2$). The group considered four potential single-carbon organic compounds
346 (HCHO , CH_3OH , CH_4 , and HCOOH). Their findings show that oxygen vacancies at the
347 surface of MXene play a crucial role in the reduction of CO_2 . They, therefore, proposed
348 that sufficient oxygen vacancies can be introduced to the MXene surface by CO and
349 H_2 . Ti_2CO_2 has the best catalytic performance for the reduction of CO_2 among the three
350 types of MXene. This computational investigation gives a new insight into the
351 emerging application of MXene in the area of photocatalytic reduction of CO_2 into
352 hydrocarbon fuels which later come to manifestation.

353 In a recent paper, for example, Li and co-authors [40] reported a ternary material
354 containing MXene as an efficient photocatalyst (**Figure 4**). According to the group
355 findings, bronze TiO₂ (TiO₂(B)) Schottky junction composites were created using Ti₃C₂
356 MXene and electrostatic self-assembly. The surface of the TiO₂(B)/Ti₃C₂ MXene was
357 then further covered with Ag₃PO₄ quantum dots through in situ self-growth, and
358 Ag₃PO₄ joined TiO₂(B) and Ti₃C₂ MXene to create heterojunctions and Schottky
359 junctions, respectively. These functional connections worked together to create the
360 photocatalyst TiO₂(B)/Ti₃C₂ MXene/Ag₃PO₄. Under the synergistic influence of these
361 functional connections, the mobility and quick separation capabilities of the
362 photogenerated electron-hole pairs of the composite photocatalyst were greatly
363 increased, and the recombination of photogenerated electron-hole pairs was
364 successfully prevented [41]. Additionally, light absorption performance has been
365 increased. As a result, the composite photocatalyst demonstrated exceptional
366 photocatalytic activity.

367 Furthermore, in the search for effective and eco-friendly semiconductor photocatalysts
368 for the reduction of CO₂ to different hydrocarbon fuels, some scientists have
369 incorporated biological enzymes into semiconductors [42]. For example, White et al.
370 [43] showed that [NiFe] CODH II from *Carboxydotherrmus hydrogenoformans* can be
371 effectively activated by light to reduce CO₂ to CO. To do this, the researchers
372 developed a hybrid photosystem combining CdSe/CdS dot-2in-rod nanocrystals and
373 CODH II. The use of a low-potential redox mediator to aid electron transport resulted
374 in quantum yields of up to 19% and turnover frequencies of 9 s⁻¹. These findings
375 establish a new standard for effectively lowering CO₂ emissions using photocatalytic
376 enzyme systems.

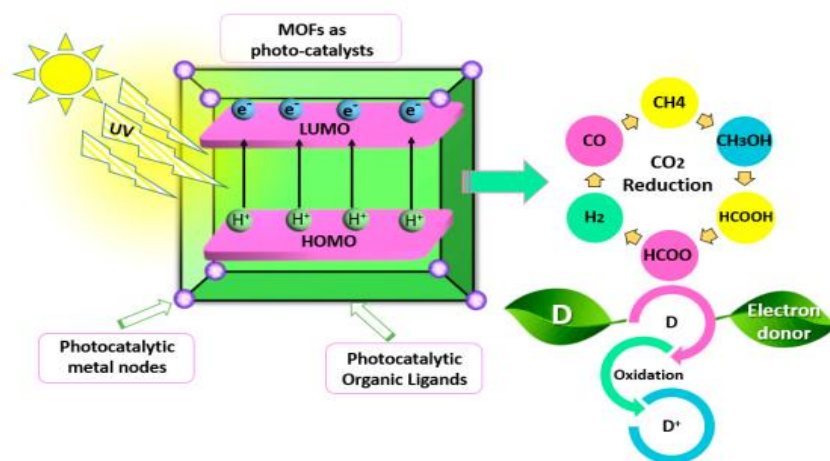


377

378 **Figure 4.** Mechanism of enhanced photocatalytic properties of semiconductor by M-
 379 Xene. Reproduced with the permission of [40]

380 6. Metal-Organic Framework Photocatalysts

381 Metal-organic frameworks (MOFs) are described as three-dimensional structures
 382 having multiple linkers as organic molecules and inorganic nodes [44,45].
 383 Fundamentally, photocatalysts are semi-conducting materials, in which upon
 384 irradiation, electrons (e^-) in the material are excited from the valence band to the
 385 conduction band[46,47]. The migration of electron, due to the reception of light energy,
 386 usually leave behind a positive vacant hole (h^+) in the valence band part of the
 387 photocatalyst as shown in **Figure 5**[48]. Here, the electron moves from HOMO
 388 (valence band) to LUMO (conduction band) and this serves as the basic feature of any
 389 semi-conducting substance like MOFs. To function effectively as a catalyst, the
 390 interfacial electron transfers as well as the separation of the e^- and h^+ requires
 391 optimization [49], else the separated charges may recombine and thus, resulting in
 392 energy-wasting process [50–52].



393

394 **Figure 5.** Separated charges on MOF for CO₂ photo-reduction process [48]

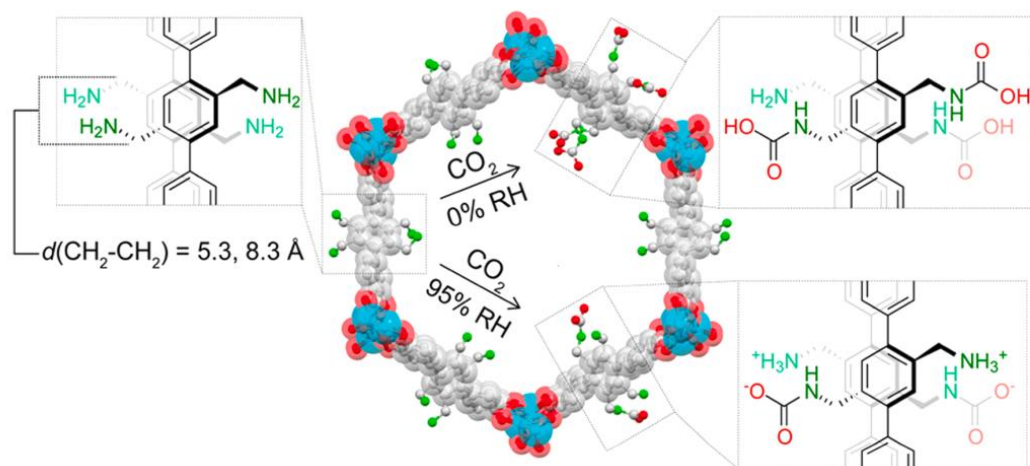
395 In chemical and petrochemical industrial processes, zeolites have found catalytic
 396 application sequel to its chemical and thermal robustness, in addition with the easy
 397 formation of the acidic site [53]. Zeolites can be synthesized and it can be found
 398 occurring naturally. In recent years, attention has shifted towards the use of synthetic
 399 form as the size and shape can be sufficiently altered to give the desired materials by
 400 simply adjusting synthesis condition like time length, temperature required for
 401 synthetic zeolite formation and Si/Al ratio [54,55]. Characteristically, zeolites have
 402 negatively charged tetrahedral aluminosily which is loosely attached to the zeolite
 403 skeletal structure and commonly counter-balanced by Group 1A or 2A elements, like
 404 Ca²⁺, Na⁺, Mg²⁺ and so on [56]. Zeolite basicity is enhanced when more aluminum
 405 atoms are present in aluminosilicate framework; and the more the basicity of zeolite,
 406 the high the capacity to capture CO₂ [57].

407 Photochemically, zeolites are inert, behave as insulating material and are therefore not
 408 excited when irradiated [58,59]. When compared, MOFs are also described as poor
 409 conductors due to the presence of organic ligand p-orbital conjugation, however,
 410 scientists have attempted to incorporate electrical conductivity into MOFs following the
 411 achievement of Allendorf in applying MOFs as microelectronic material [60]. MOFs
 412 are characterized as hybrid materials with tunable structure which confers on them
 413 versatility than any organic or inorganic semi-conducting materials [60,61]. The light
 414 absorbing portion of MOFs can be linked to the organic linkers that are connected to
 415 the inorganic part of MOFs (metal nodes); here, the organic linkers are receptive to
 416 light and induce the activation of quantum dots [62]

417 The photocatalytic properties are exhibited, just as in the case of semiconductors, via
418 ligand-to-metal-charge transfer (LMCT) and $\pi \rightarrow \pi^*$ electron transition in organic
419 linkers in the visible (400-800 nm) and ultraviolet (200-400 nm) region of the
420 electromagnetic spectrum, similar to semiconductors [63]. Pure zeolite, on the other
421 hand, are only capable of absorbing light at wavelength lower than 220 nm [64]. Garcia
422 et al. investigation into the property of MOFs confirmed the semiconducting features of
423 MOFs via LMCT which resulted into separation of charges to form e^- and h^+ [65].
424 They found that photoinduced electron transfer processes to viologen produces the
425 corresponding viologen radical cation, while holes of MOF-5 were effective at
426 oxidizing N,N,N',N'-tetramethyl-p-phenylenediamine. The detection of delocalized
427 electrons was observed by using laser flash photolysis technique, revealing
428 microseconds residence time of electrons in the conduction band (CB). Findings have
429 revealed that, besides LMCT, $\pi \rightarrow \pi^*$ in MOFs ligand is suggested as a feasible
430 mechanism for the semiconducting properties of some MOFs [66,67].

431 6.1 CO₂ capture by MOFs

432 The simultaneous capturing and storage of carbon dioxide as well as its transformation
433 to fuels are now the primary focus of research in CO₂ reduction, in order to tackle the
434 global climate change [68–71]. The dominant capturing approach is via chemisorption
435 onto the functionality on the MOFs. Flaig and coworkers observed that there was 2.3
436 times increment in the capturing of CO₂ by IR-MOF-74-III-CH₂NH₂ at lower CO₂
437 pressures and it as ascribed to promotion of chemisorption of CO₂ due to the presence
438 of two alkyl-amines per organic linker in the MOF [72]. **Figure 6** shows a typical
439 mechanism for CO₂ capture by IR-MOF-74-III-(CH₂NH₂)₂. The three basic approaches
440 employed by using MOFs for the reduction of CO₂ emission coming from fuel
441 combustion in power plants oxy-fuel combustion, post-combustion and pre-combustion
442 capturing [48] The choice of any of the aforementioned methods solely depends on a
443 number of factors like CO₂ concentration and its partial pressure in flue gas, and the
444 merits and demerits of each of the approach. The comparison of the approaches is
445 presented in **Table 1**.



446

447 **Figure 6.** Schematic representation of mechanistic CO₂ capture by IR-MOF-74-III-
 448 (CH₂NH₂)₂ (Mg₂(2',5'-bis(aminomethyl)-3,3''-dioxido-[1,1':4',1''-terphen-yl]-4,4''-
 449 dicarboxylate) Adapted with the permission [72]. Copyright (2017) Elsevier

450 **Table 1.** Merits and demerits various approached for CO₂ capture [48]

Merits			
Entry	Post-combustion	Pre-combustion	Oxy-combustion
1.	Frequently employed methods in CO ₂ capture	Less volume of water is required in this process, compared to post-combustion method	No need for onsite-operation and can fit into an existing power plant
2.	Plant efficiency is enhanced and CO ₂ emissions reduced due to development of powdered coal systems	Synthetic gas can find application in powering turbine cycle	It requires a low-cost to capture CO ₂ . For instance, more than of CO ₂ can be captured by this low-cost approach
3.	Research and developments are ongoing to further improve the adsorption capacity of adsorbents and capturing instrument	This approach requires a low-energy for CO ₂ capture compared to other methods	Pollutants released by this approach are at low-cost.
4.	Suitable for current and future coal-powered power plants	Often applied in industries	Large volumes of steams are generated

Demerits			
Entry	Post-combustion	Pre-combustion	Oxy-combustion
1.	The efficiency is negatively affected due to steam extraction that reduce the flow into turbine	Supporting systems extensively needed	Scaling-up requires further findings or experiments
2.	For high CO ₂ capture, this method requires large volume of water and a high circulation volume.	Only suitable for new power plants	Leakage of CO ₂ is most possible
3.	At ambient condition, the partial pressure of CO ₂ is low	In this method, energy is majorly lost	High energy is needed
4.	Reduction in efficiency as a result of application of amine technologies in this approach	Expensive to procure equipment	Overall, it is not cost-effective

451

452 Previous studies have reported the features of MOFs that are suitable for CO₂ capture.
 453 For instance, it was mentioned that MOF for CO₂ capture should have enhanced
 454 porosity, CO₂ adsorption capacity and selectivity [73]. Also, the authors mentioned that
 455 a perfect material for CO₂ capture should possess an extremely reduced uptake ability
 456 for other gasses like nitrogen and methane, when compared with its adsorption capacity
 457 for CO₂ [73] According to Kang et al. in any industrial process involving the separation
 458 of gases, it is usually a challenging task. However, MOFs have proven to be suitable
 459 materials to be used in gas separation applications in industries [74]. MOF materials'
 460 unique structural and chemical features, such as pore porosity, open metal sites, and
 461 polar functional groups in the pore channel size, have informed their effectiveness in
 462 capturing CO₂ [75] **Table 2** presents some examples of MOFs, their CO₂ uptake
 463 capacity and operating conditions.

464 **Table 2.** A compiled list of some MOFs and the adsorption capacity for CO₂

Entry	Type of MOFs	Operating conditions	CO ₂ adsorption capacity	References
1.	UMCM-1-NH ₂ -	T=25 °C; P= 18 bar	19.8 mmol/g	[76]

	MA			
2.	A core-shell MOF	T=0 °C; P= 1 bar	41 mmol/g	[77]
3.	HCM-Cu ₃ (BTC) ₂₋₃	T=25 °C; P= 1 bar	2.8 mmol/g	[78]
4.	(ZIF-20)	T=0 °C; P= 760 Torr	70 mL/g	[79]
5.	Zn(adc) (4,40-bpe) _{0.5}	T= -78.15 °C; P= 1 p/p	130 mmol/g	[80]
6.	Zn(II)-based MOFs	T=25 °C; P= 1 bar	9.2 mmol/g	[81]
7.	(PCN-5)	T = -78.15 °C; P = 760 Torr	210 mg/g	[82]
8.	SNU-110	T = 78 °C; P = 1 bar	6 mmol/g	[83]
9.	Cu(dhbc) ₂ (4,40-bpy)	T=24.85 °C; P=0.4~8 atm	70 mL/g	[84]
10.	Cu(pyrdc)(bpp)	T = -78.15 °C; P = varies	varies	[85]
11.	MOF with PEI	T = 78 °C; P = 0.15 bar	4.2 mmol/g	[86]
12.	[Ni(bpe) ₂ (N(CN) ₂)] (N(CN) ₂)	T= -78.15 °C; P = 1 p/p	35 mL/g	[85]
13.	Cu(bdc) (4,40-bpy) _{0.5}	T=24.85 °C; P = 0.10 MPa	70 mL/g	[84]
14.	MIL-53 with BNH _x	T = 0 °C; P= 1 bar	4.5 mmol/g	[87]
15.	(MIL-53)	T = 30.85 °C; P = 20 bar	7.5 mmol/g	[88]
16.	NJU-Bai12	T = 0 °C; P = 20 bar	28.3 mmol/g	[89]
17.	Cu(fam) (4,40-bpe) _{0.5}	T = -78.15 °C; P = 760 torr	100 mL/g	[90]

465

466 **6.2 The utilization of MOFs in CO₂ photoconversion**

467 Photo-conversion also known as photocatalysis are basically catalytic reactions that
468 occurs under the influence of sunlight [91]. Metal organic frameworks which comprise
469 of a metal linked to organic ligands to form a well-coordinated network are often used
470 as photocatalyst for CO₂ conversion due to their promising potentials to solve
471 environmental problems associated with CO₂ release. Other conventional

472 photocatalysts such as semiconducting compounds (e.g., Zn_2GeO_4 , Zn_2GeO_4 , CdS) that
473 incorporates a metal-zeolite framework have lower performance due to lower efficiency
474 of charge separations, surface area and weak adsorption capacity for CO_2 [92]. In
475 contrast, MOFs are known to be a good material for CO_2 conversion because the
476 framework supports high absorption of photons due to electrophilic aromatic polymeric
477 species present in the structure following electron transfer from the organic ligands to
478 the central atoms thus leading to charge separation of localized excitons [64,93].
479 Another thrilling discovery is that the adsorptive potentials of MOFs can be enhanced
480 by utilization of light harvesting components which can be synthesized using a visible
481 light-sensitive metal like iron (Fe) [94]. However, this might affect their adsorptive
482 capacity and CO_2 selectivity in aqueous media, gases and acid
483 [95]. Organic components or linkers used for light harvesting responds to light due to f
484 actors like functionality e.g., 2aminoterephthalic acid, or inclusion of photoreactive met
485 alloligands[94,96].
486 Furthermore, due to the porous structure of MOFs, photosensitive materials can be
487 incorporated into the cavity's framework which is quite difficult to achieve in other
488 semiconductor catalysts such as Zn_2GeO_4 , CdS since the photosensitive sites are
489 dispersed on the exterior surface of the complex instead of the structure's cavity
490 [92,97]. In addition to this, the immobilization of the photoactive sites in the linker
491 coupled with the cavity structures and metal mode of MOFs makes them a suitable
492 candidate for a lot of applications especially when designing smart materials that are
493 sensitive to external stimuli. This potential characteristic makes them more versatile in
494 use compared to zeolites[92,98]. Even though several efforts have been put into the
495 optimization of the photolytic performance of MOFs, some milestones are yet to be
496 covered.

497 **6.2.1 Mechanism of CO_2 photo-reduction by MOFs**

498 CO_2 photo-reduction takes place in the presence of light (200-800 nm). This reduction
499 can lead to the formation of CH_4 , CO, HCHO, and CH_3OH , depending on the reduction
500 potential [75] (see **Table 3**). The photo-reduction of CO_2 occurs in a series of steps as
501 follows. The CO_2 pollutant is adsorbed on a photocatalyst like MOFs, there is
502 formation, separation and transportation of charge carriers (photo-hole and
503 photoelectron) and the surface species (CO_2) react with the formed charges to form
504 various products depending on reduction potential needed for a particular product to be

505 formed [99,100]. As a result of the interaction of the photo-hole and photo-electron
 506 forms, photocatalysts with low bandgap and high redox potential are suitable for CO₂
 507 photo-transformation. With the use of MOFs, light is first absorbed by the photocatalyst
 508 (MOFs) resulting in charge (photohole-photoelectron) separation via excitation of
 509 electron from the highest occupied molecular orbital of organic linkers in MOFs
 510 (HOMO) to the lowest unoccupied molecular orbital of organic linkers in MOFs
 511 (LUMO) [101]. Subsequently, the adsorbed CO₂ consumes the electrons formed (in the
 512 LUMO) to form different categories of value-added products such as CO, CH₄, CH₃OH
 513 and HCOOH.

514 **Table 3:** Various standard reduction potentials of CO₂

Entry	Reduction potentials	Normal hydrogen electrode vs reduction potential (V)
1.	$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.24
2.	$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.48
3.	$\text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	+0.41
4.	$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38
5.	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.53
6.	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.61
7.	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOO}^-$	-0.49

515

516 **6.2.2 Challenges of MOFs synthesis and application**

517 The chemical and thermal instability of MOF photocatalysts during synthesis is a
 518 significant issue. At temperatures above 250°C, several MOFs break down during
 519 synthesis. Because of interactions with species that contain nucleophiles in the
 520 synthetic chemicals, the network structure may become unstable [102,103]. A few
 521 examples of such nucleophilic substances are amines and alkoxide. The potential for
 522 photochemical instability that results from extended exposure to the metal-organic
 523 network to irradiation and causes photo-oxidation of the organic moiety of the

524 framework is another aspect that hinders MOFs' performance. Therefore, it is essential
525 to pay attention to this material's photostability when exposed to light [64]. This might
526 be done by running a timed-control experiment to determine the exact time allowance
527 for the MOFs of interest, then utilizing spectroscopic methods and the X-ray diffraction
528 (XRD) method to confirm the stability.

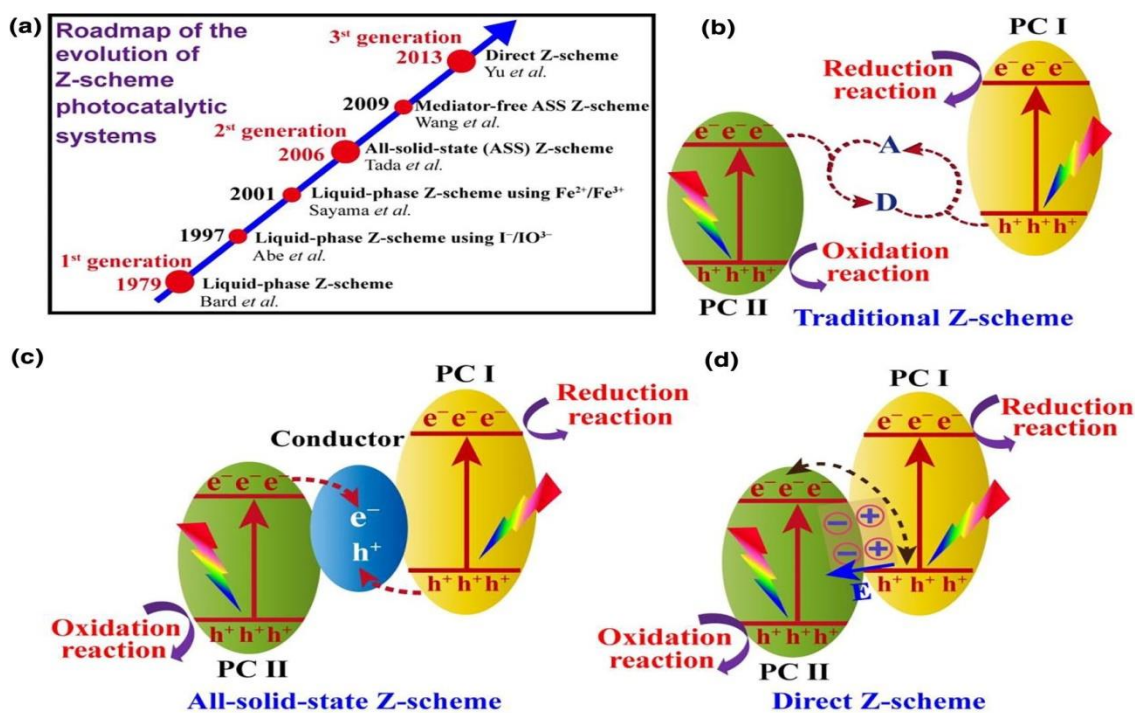
529 **7. Z-scheme photocatalysts**

530 The natural process of photosynthesis, in which photogenerated electrons are carried
531 through a Z-scheme mode, allows green plants to efficiently convert CO₂ and H₂O to
532 O₂ and carbohydrates [104]. An artificial Z-scheme photocatalyst with higher potential
533 for generating high photocatalytic performance in CO₂ reduction is one that was
534 inspired by this natural photosynthesis process [105]. The artificial Z-scheme
535 photocatalyst usually consists of two semiconductors. The roadmap for the historical
536 evolution of Z-scheme photocatalysts [106] and different charger transfer routes of Z-
537 scheme family are presented in **Figure 7**. In summary, Z-scheme photocatalysts can be
538 divided into three generation [105] (1) First generation: traditional Z-scheme
539 photocatalysts in redox ion pairs such as Fe³⁺/Fe²⁺ is used as medium for charge
540 carriers (2) Second generation: all solid state Z-scheme photocatalysts in which
541 electron conductor such as platinum nanoparticles is employed to serve as charge
542 transfer medium (3) Third generation: direct Z-scheme photocatalysts, in which the
543 charge carrier transfer is mediated by an internal electric field rather than a third party
544 and a direct contact between two semiconductors is ensured.

545 It is important to mention that high stability for water oxidation is one benefit of
546 semiconductors but low selectivity for CO₂ reduction is one major drawback
547 (accompanied with H₂ evolution). A molecular metal complex, in contrast, has
548 moderate ability for oxidation process under the condition of photocatalytic CO₂
549 reduction but good selectivity for photo- and electrochemical CO₂ reduction. With
550 these advantages and disadvantages of metal complexes and semiconductors in
551 photocatalytic CO₂ reduction systems in mind, it seems likely that a hybrid system with
552 a metal complex and a semiconductor acting as the reduction and oxidation centers,
553 respectively, could function as an efficient visible-light photocatalyst for CO₂ reduction
554 with high selectivity using water as the electron source. In aqueous environments, the
555 performance of such metal-complex/semiconductor hybrid systems could be improved

556 by anchoring water-insoluble metal-complex (photo)catalysts to solid surfaces to avert
 557 unfavorable aggregation [107].

558 This section focuses on scientific literature on two semiconductors and hybrid
 559 photocatalysts for CO₂ reduction. One of the earliest research works on Z-scheme
 560 (metal-complex/semiconductor) was reported by Sato and co-workers [108] in the year
 561 2015. The team demonstrated a semiconductor/metal-complex hybrid photocatalyst for
 562 selective CO₂ reduction, employing the metal complex catalyst [Ru(dcbpy)₂]Cl₂([Ru-
 563 dcbpy]) (dcbpy =4,4'-dicarboxy-2,2'-bipyridine) with electrocatalytic CO₂ reduction.
 564 The Z-scheme approach, at least in theory, can solve both the poor reduction
 565 performance of semiconductor photocatalysts and the poor oxidation ability of metal-
 566 complex photocatalysts. Because less energy is needed to drive CO₂ reduction and
 567 water oxidation than in a one-step photoexcitation system, a Z-scheme system can
 568 utilize a wider range of visible light. Both the metal complex and the semiconductor
 569 components have a significant impact on the photocatalytic performance of such two-
 570 reaction schemes. Therefore, the development of metal complexes and semiconductors
 571 is crucial. **Table 4** lists some of the recently developed metal-complex/semiconductor
 572 hybrid systems for CO₂ reduction using visible light photocatalysis and photo-
 573 electrochemistry.



574

575 **Figure 7.** (a) Roadmap for the of evolution of Z-scheme photocatalysts (b) Traditional
 576 Z-scheme charge transfer mechanism (c) All-solid-state Z-scheme charge transfer
 577 mechanism (d) Direct Z-scheme charge transfer mechanism. Adapted with the
 578 permission [105] . Copyright (2018) Elsevier.

579 **Table 4.** Z-scheme metal complex/semiconductor hybrid system for the reduction of
 580 CO₂ by photocatalysis and photoelectrochemistry driven by visible light

Z-scheme Photocatalysts	Cocatalysts	Conditions	Yield (%)	Catalyst dose (mg)	Main product	Remarks	Ref.
TaON and Ta/N-co-doped in conjunction with a binuclear (II) complex, GaN:ZnO solid solutions	Ag	300W xenon lamp; $\lambda > 400$ nm; 365 nm; 15h; pH:6.4	-	4	Hydrogen and formate	It demonstrates the huge potential of band-tunable mixed-anion semiconductors as components of Z-scheme hybrid photocatalysts for CO ₂ reduction via visible light.	[10, 9]
Copolymerized carbon nitride with Ru (II) complex	polymer	300W xenon lamp; $\lambda > 500$ nm; 5h	98	20	Formic acid	The study unmistakably demonstrated that, even without the need for the labor-intensive postsynthesis modifications typically used to increase electron density, a straightforward modification of a bulk	[11, 0]

					semiconductor through the copolymerization approach becomes another efficient way to increase the photocatalytic activity of the hybrid photocatalyst.
Ru-complex Ta ₂ O ₂ (N-nitrogen doped Ta ₂ O ₅) hybrid	NH ₃	500W xenon lamp; λ>390 - 750 nm; 15h; pH:5-6	10	Carbon monoxide and formic acid	The research contends that NH ₃ adsorption on the surface facilitates electron transport from the Ta ₂ O ₅ to the Ru-complex. Additionally, it appears from the calculations done in this work that the replacement of NH groups for surface oxygen atoms causes Ta ₂ O ₅ 's absorption band edge to shift red, but the CBM to shift upward just slightly [11]
Macrocyclic Co(III) on three different semiconductor or surfaces	No	mercury lamp; λ>420 nm; 5h	10		Because N-Ta ₂ O ₅ -based hybrid photocatalysts lack surface functionalities (such as hydroxyl groups) necessary for the molecular deposition of cobalt complexes, they exhibit poor activity. [11]
Mesoporous	Polym	300W	60 8	Carbon	To achieve photocatalytic [11]

carbon nitride with polymeric cobalt phthalocyanine catalyst	er	xenon lamp; $\lambda > 500$ nm; 5h		monoxide	CO ₂ conversion, the in situ polymerization of the phthalocyanine is essential because it enables control over the catalyst loading.	3]
Mn-immobilized TiO ₂ hybrid (OrgD-[TiO ₂]-MnP)	Dye	60W LED lamp; $\lambda \geq 400$ nm; 23h	> 10 99	Formate and carbon monoxide	The amount of MnP loaded onto the surface of TiO ₂ was discovered to be a key factor in controlling the product selectivity (HCOO ⁻ /CO)	[11 4]
Ir X ⁺ immobilized on ReC anchored TiO ₂ hybrid catalyst	Ir (III) complex	60W LED lamp; $\lambda > 400$ nm	- 10	Carbon monoxide	This study establishes that Ir-X ⁺ can function in solution as an efficient and reliable photosensitizer for the CO ₂ reduction based on the TiO ₂ /ReC binary catalyst. It also suggests that the structure-reactivity relationships investigated in this study may provide a strategic basis for the molecular design of Ir-complex-based photosensitizers that will lead to the creation of effective and long-lasting CO ₂ reduction systems.	[11 5]

581 OrgD = Organic sensitizer [4,4'-bis(diethoxyphosphorylmethyl)-2,2'-bipyridine], MnP
582 = Manganese complex, ReC = Re(4,4'-Y₂-bpy)(CO)₃Cl (ReC = ReP; Y = CH₂PO₃H₂)
583 and CBM: Conduction band

584 Very recently, conscious efforts have been made to explore the possibility of two
585 semiconductors Z-scheme two-step photoexcitation approach to reduce CO₂ using
586 water as the electron source in a powder-based suspension system or without sacrificial
587 reagent. For example, Huang et al. [116] successfully developed a typical type II
588 heterojunction utilizing composite materials made of In₂S₃/TiO₂. They discovered that
589 a high separation efficiency of the photogenerated electron-hole pairs has been attained
590 by adjusting the In₂S₃/TiO₂ ratio. Without the use of an extra sacrificial agent, it was
591 found that 5 % In₂S₃/TiO₂ demonstrated a CH₄ generation rate of 16.21 μmol g⁻¹ h⁻¹,
592 and the catalytic activity is significantly higher than that of pure TiO₂ nanosheets. The
593 large specific surface area and improved visible light harvesting of the hybrid catalyst
594 were both credited with its high catalytic activity. In another study, Che and co-workers
595 [117] demonstrated that Z-scheme g-C₃N₄/Ag₂CrO₄ photocatalysts exhibited excellent
596 hydrogen evolution efficiency in comparison with the individual Ag₂CrO₄ and g-C₃N₄
597 under visible light irradiation (420 nm). They found that by optimizing the In₂S₃/TiO₂
598 ratio, a high separation was achieved. The composite that had the best mass-to-volume
599 ratio, 23.1%, had the highest photocatalytic activity, which was 902.1 μmol g⁻¹ h⁻¹. The
600 creation of the Z-scheme g-C₃N₄/Ag₂CrO₄ heterostructures, which had greater
601 separation and transfer efficiencies of the photogenerated electron-hole pairs, is
602 credited with the increased photocatalytic activity. Additionally, the photocorrosion of
603 Ag₂CrO₄ nanoparticles was significantly reduced due to the firm coupling of Ag₂CrO₄
604 and g-C₃N₄ in heterostructures. This research may bring fresh insights into the design
605 of Z-scheme heterostructures and contribute to our understanding of the mechanism of
606 g-C₃N₄/silver composites. In a related study, Sun et al. [118] reported type II
607 heterostructure of In₂O₃/BiOI spherical nanosheets as a promising photocatalyst for the
608 reduction of CO₂. The group found that the improved BI-10 had the highest
609 photocatalytic yields, with CO and CH₄ yields of 11.98 mol g⁻¹h⁻¹ and 5.69 mol g⁻¹h⁻¹,
610 respectively. As well as being 5.3 and 4.2 times higher than pure BiOI and pure In₂O₃
611 and 2.1 and 1.9 times higher than pure BiOI and pure In₂O₃, respectively, the yields of
612 CO and CH₄ were also greater. This is explained by the type II heterojunction formed
613 by the close contact of In₂O₃ and BiOI, which broadens the photoreaction's spectral

614 range and facilitates effective charge separation and transfer at the heterojunction
615 interface. This research can serve as a model for catalyst modification that is generally
616 applicable to photocatalysis.

617 A shuttle redox mediator was discovered to promote electron transfer between two
618 semiconductors in these systems. Because of its numerous advantages, the
619 semiconductor-based Z-scheme approach has become a popular candidate in
620 photocatalytic CO₂ reduction research, but especially in water splitting. These include
621 the ability to separate reduction/oxidation products as well as the use of a broader range
622 of visible light. Furthermore, semiconductors with a reduction potential suitable for
623 either CO₂ reduction or water oxidation can be used on each side of the system.

624 However, difficulties with thermodynamics, charge-transfer dynamics, applicability
625 and practical synthesis are faced by all types of Z-scheme heterojunction. In this case, it
626 is preferable to substitute Z-scheme in favour of a fresh idea that explicitly explains the
627 mechanism of the photocatalytic CO₂ reduction reaction (PCRR).

628 **8. S-scheme**

629 To overcome the limitations of the Z-scheme heterojunctions, Yu and his colleagues
630 [119] proposed a new step-scheme abbreviated as S-scheme heterojunction. This S-
631 scheme heterojunction is made up of staggered band structures of reduction
632 photocatalyst (RP) and oxidation photocatalyst (OP) which is similar to type II
633 heterojunctions but with an absolutely different pathway of charge transfer. Unlike
634 other types of heterojunctions, the RP of S-scheme photocatalyst is constructed with
635 higher CB and VB levels and smaller work function compared to OP (**Figure 8a**).
636 According to the review paper of Xu et al. [120], the charge transfer pathway of S-
637 scheme heterojunction can be explained in three steps as thus; (1) When OP and RP
638 interact, electrons in the RP randomly disperse to OP, resulting in layer depletion and
639 layer accumulation close to the interface in RP and OP, as shown in **Figure 8a**. The OP
640 becomes more negatively charged, while the RP becomes more positively charged, and
641 an internal electric field directing from the RP to the OP is formed at the same time
642 (**Figure 8b**). This internal electric field accelerates the transfer of photogenerated
643 electrons from OP to RP (2) When the two semiconductors touch, their Fermi energy
644 levels align to the same level, which causes an increase and decrease, respectively, in
645 the Fermi levels of OP and RP (**Figure 8c**). (3) Due to the Coulombic attraction

646 between the holes and electrons, the photogenerated e^- in the CB of the OP and the h^+
647 in the VB of the RP are inclined at the interface. In summary, electron recombination in
648 the CB of OP and hole recombination in the VB of RP are driven by three factors
649 including the internal electric field, band bending and Coulombic attraction. Therefore,
650 the powerful photogenerated electrons in the CB of RP and the holes in the VB of OP
651 are preserved to take part in the PCRR while the useless electrons and holes are
652 eliminated via recombination. It is important to note that the S-scheme heterojunction is
653 suitable for PCRR because the reserved photogenerated electrons and holes are
654 spatially separated and have significant redox abilities because of the diversified
655 charge-transfer mode.

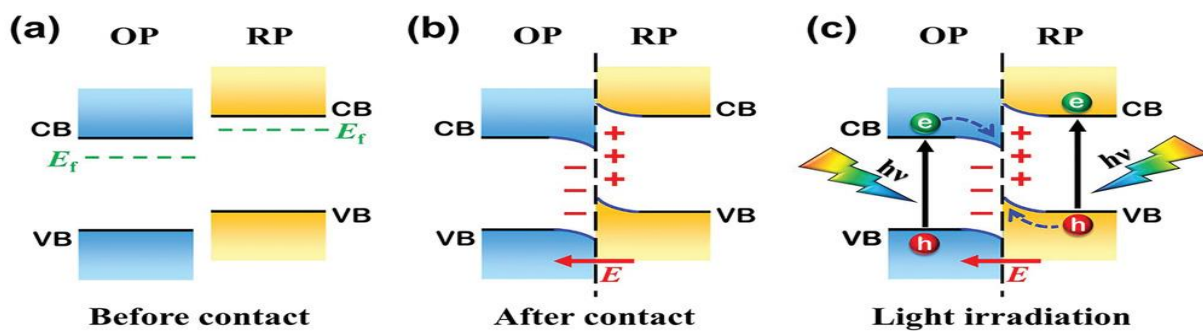
656 Considering the dynamic and unambiguous charge transfer mechanism, strong redox
657 ability and accelerate electrons and holes of S-scheme heterojunction, researchers have
658 developed strong interest particularly for PCRR. For instance, Zhang et al. [121]
659 reported a novel S-scheme composite consisting of ultrasmall copper phosphosulfide
660 (us-Cu₃P|S) nanocrystals anchored on 2D g-C₃N₄ nanosheets synthesized via a wet
661 chemical method. The estimated work function (ϕ) of g-C₃N₄ and us-Cu₃P|S are 3.93
662 and 5.16 eV. The group claims that the Fermi levels of g-C₃N₄ and us-Cu₃P|S shift to
663 the same energy level of 0.52 V when they are coupled, adjusting the band positions of
664 the us-Cu₃P|S/CN composite (**Figure 9**). Such band alignment of g-C₃N₄ and us-Cu₃P|S
665 permits either type-II heterojunction or S-scheme interfaces, leading to two distinct
666 electron transfer pathways. According to the S-scheme mechanism, it is possible that
667 g-C₃N₄ conducts the H₂O oxidation reaction while us-Cu₃P|S conducts the CO₂
668 reduction reaction because the VB position of us-Cu₃P|S in the composite is below the
669 O₂/H₂O standard redox potential. In a nutshell, us-Cu₃P|S and g-C₃N₄ interact to form
670 an S-scheme heterojunction that serves as an electron transfer channel and promotes the
671 separation and migration of photogenerated charge carriers by forming interfacial P-N
672 chemical bonds. As a result of the altered band structures of us-Cu₃P|S and g-C₃N₄
673 during composite formation, a photocatalytic CO generation rate of 137 $\mu\text{mol g}^{-1} \text{h}^{-1}$
674 which is eight times higher than that of pristine g-C₃N₄ is produced.

675 Aside from the previously mentioned 2D architecture g-C₃N₄, Wang and his colleagues
676 [122] carefully encapsulated ZnIn₂S₄ nanosheets on the outer layer of TiO₂ hollow
677 spheres in order to create a 1D hierarchical S-scheme TiO₂@ZnIn₂S₄ heterojunction for
678 improved PCRR. The in situ irradiated x-ray photoelectron spectroscopy, electron

679 paramagnetic resonance and work function analysis demonstrate S-scheme charge
680 transfer mechanism (**Figure 10**). When compared to regular pristine ZnIn_2S_4 and TiO_2 ,
681 S-scheme $\text{TiO}_2@ZnIn_2S_4$ heterojunction photocatalyst performance is significantly
682 improved. S-scheme $\text{TiO}_2@ZnIn_2S_4$ heterojunction's total CO_2 photoreduction
683 conversion rates (the sum yield of CO , CH_3OH and CH_4) increased by 2.75 and 4.43
684 times, respectively. According to experimental results, this logical design offers a lot of
685 active sites and large surface areas for multi-electron PCRR as well as effectively
686 separating useful photogenerated electrons and holes.

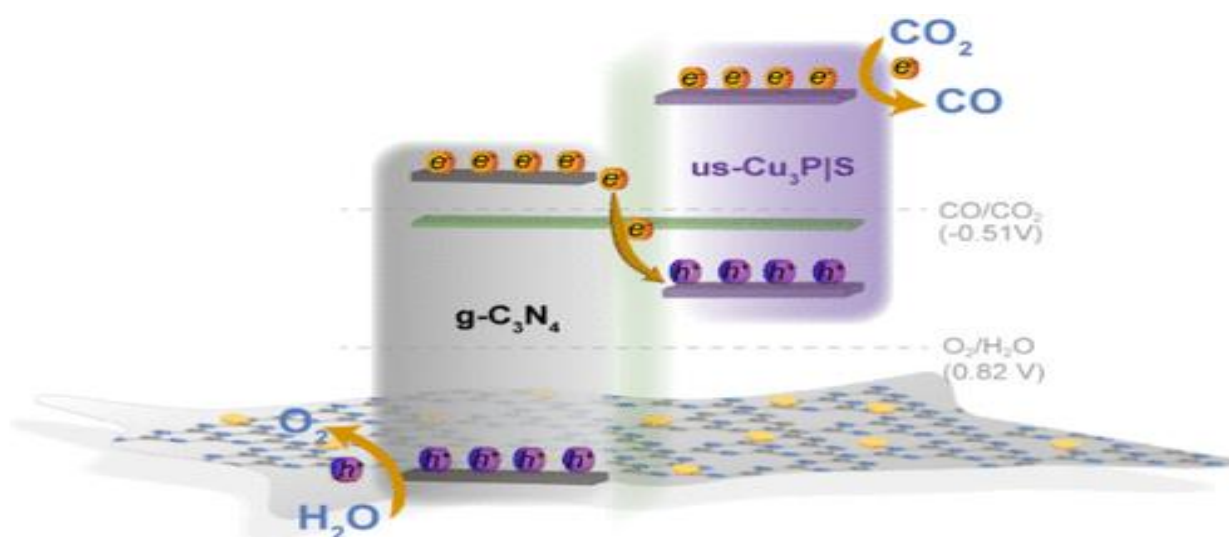
687 In another recent study, a group of researchers [123] developed a novel S-scheme
688 heterojunction of CsPbBr_3 nanocrystals/ CoAl layered double hydroxide nanosheets
689 composite as an efficient photocatalyst for CO_2 reduction (**Figure 11**). The S-scheme
690 heterojunction not only allowed photogenerated electron/hole pairs to separate, but it
691 also kept CB photoinduced reducing ability on the CsPbBr_3 . Additionally, the increased
692 CO_2 adsorption and activation were significantly improved in the PCRR compared to
693 single photocatalyst. The CPB/LDH composite demonstrated significantly improved
694 photocatalytic properties in PCRR as a result of these synergistic actions. The 0.6
695 CPB/LDH sample had the highest activity, with quantum yield of 59.5 mol.g^{-1} ($\text{CO} +$
696 CH_4) which were 9.9-fold higher than the original CoAl-LDH and 2.6-fold higher than
697 CsPbBr_3 . Wang et al. recently reported hierarchical hollow structured S-scheme
698 photocatalysts of TiO_2 nanosheet arrays-decorated In_2O_3 hexagonal nanotubes by in-
699 situ hydrothermal method [124]. The team discovered that the $\text{In}_2\text{O}_3@TiO_2$
700 photocatalyst internal electric field acts as a powerful driving force for the S-scheme
701 electron transfer from the CB of TiO_2 to the VB of In_2O_3 . For the selective
702 photocatalytic conversion of CO_2 with H_2O into hydrocarbon fuel (CH_4) without the
703 use of a sacrificial agent, the $\text{In}_2\text{O}_3@TiO_2$ catalysts demonstrated outstanding
704 performance. The S-scheme with the highest selectivity (88.1%) and yield (11.1 mol g^{-1}
705 h^{-1}) of the CH_4 product is $\text{In}_2\text{O}_3@TiO_2-10$ among all the tested photocatalysts.

706



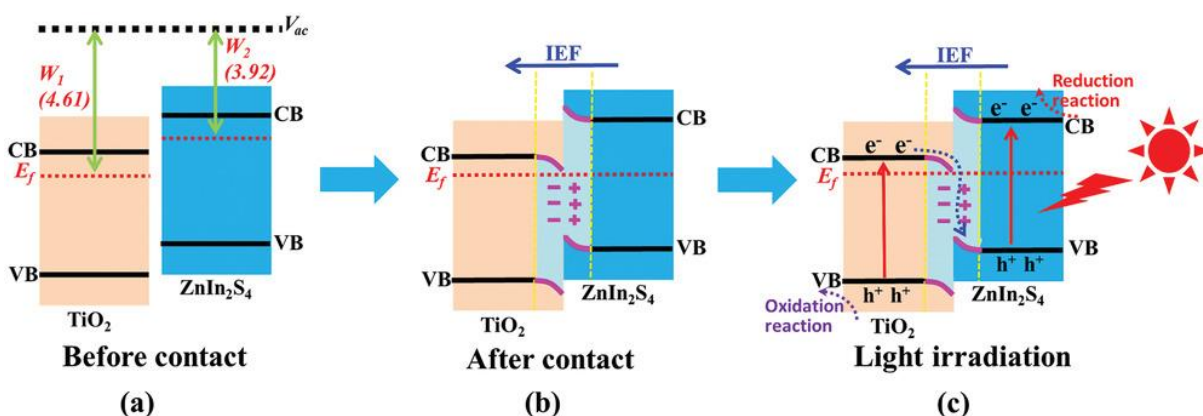
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Figure 8: Mechanism of charge transfer in S-scheme heterojunction. Adapted with the permission from ref. [125]. Copyright (2022) Wiley Online Library.



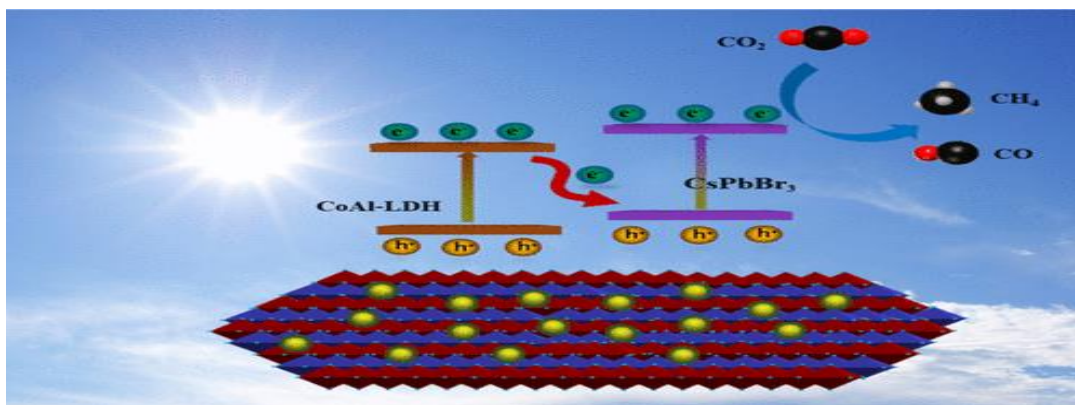
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711 Figure 9: Charge transfer route of us-Cu₃P|S/CN S-scheme heterojunction under
712 irradiation. Adapted with the permission from ref.[121]. Copyright (2021) American
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714

715 Figure 11: Charge transfer mechanism of hierarchical S-scheme TiO₂@ZnIn₂S₄
716 heterojunction. Adapted with the permission from ref. [122]. Copyright (2021) Wiley
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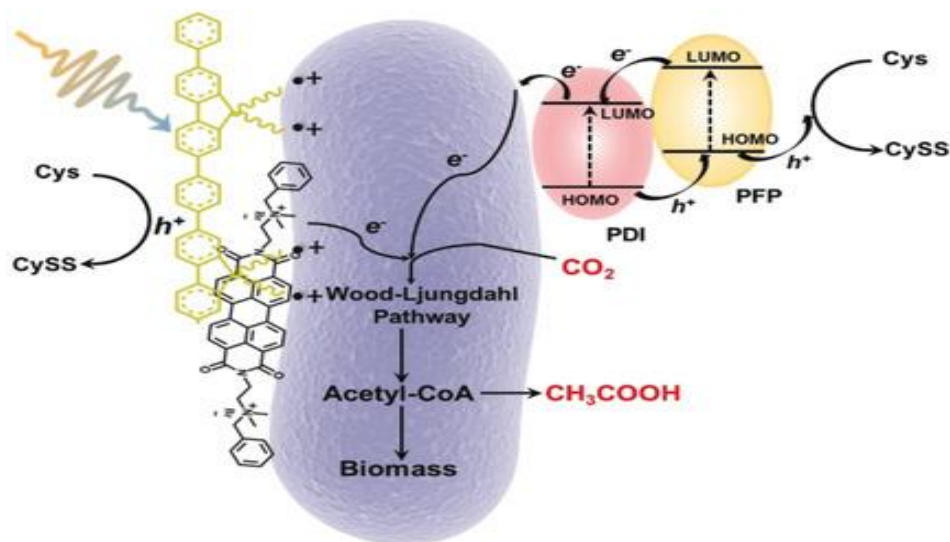
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719 Figure 11: Mechanism of PCRR by CPB/LDH S-scheme heterojunction under
 720 irradiation. Adapted with the permission from ref.[123]. Copyright (2022) American
 721 Chemical Society

722 9. Organic photocatalysts

723 Without a brief overview of recent studies using microbes or organic materials as
 724 effective photocatalysts for CO₂ reduction, this review exercise would not have been
 725 completed. Photosynthetic biohybrid systems, which combine the remarkable light-
 726 harvesting abilities of semiconductors with the capacity for biological cells to
 727 synthesize energy, have become a promising platform for solar-to-chemical conversion.
 728 In recent time, Gai and co-authors [126] invented a non-photosynthetic bacteria called
 729 *Moorella thermoacetica* that efficiently reduces CO₂ to create acetic acid through an
 730 organic, π -conjugated semiconductor–bacteria biohybrid photosynthetic system (see
 731 **Figure 12**). In order to form a p-n heterojunction (PFP/PDI layer), which offers a
 732 higher hole/electron separation efficiency, both cationic electron-transporting (n-type)
 733 perylene diimide derivative (PDI) and hole-transporting (p-type) poly(flourene-co-
 734 phenylene) (PFP) molecules were coated on the surface of the bacteria as
 735 photosensitizers. The cationic side chains of organic semiconductors might intercalate
 736 into cell membranes, assuring the effective electron transmission to bacteria.
 737 Additionally, the π -conjugated semiconductors have high light-harvesting capacity and
 738 biocompatibility. *Moorella thermoacetica* is able to utilize photoexcited electrons from
 739 the PFP/PDI heterojunction in order to activate the Wood-Ljungdahl pathway to
 740 produce acetic acid from CO₂ in the presence of light. This organic biohybrid's
 741 efficiency of 1.6% is comparable to that of previously reported inorganic biohybrid
 742 systems. In addition to opening up a new area for research into organic semiconductor
 743 applications in bioenergy, this work also offers a practical biomanufacturing method for

744 creating organic semiconductor–bacteria biohybrids for effective solar–to–chemical
745 conversion.



746

747 Figure 12. Organic semiconductor-bacteria biohybrid photosynthetic pathway [126]

748 10. Conclusions and future outlook

749 Metal-organic frameworks, metal complexes, semiconductors, Z-schemes and organic
750 photocatalysts designed for the reduction of CO₂ under visible light irradiation are
751 reviewed. Furthermore, in order to produce a balance report, the review surveys
752 computational studies on some of the aforementioned material. According to the
753 literature, certain metal-organic frameworks, metal complexes, and semiconductors can
754 function as suitable photocatalysts for CO₂ reduction with high selectivity and superior
755 turnover number, producing desired products such as CO, CH₄, CH₃OH, HCOOH or
756 HCOO⁻. Overall, the findings demonstrate that metal-complex photocatalysts are most
757 effective when immobilized on a semiconductor with a sufficiently negative
758 conduction-band potential. Weaker electron donors that cannot be oxidized by the
759 metal complex can be used as a result of this immobilization. Therefore, these metal
760 complex/semiconductor hybrid photocatalysts outperform equivalent single-component
761 systems having only a metal complex or a semiconductor under the identical reaction
762 circumstances. The same outstanding synergistic effect was also reported for Z-scheme,
763 MOFs and organic composites though with some unresolved challenges of charge
764 transfer particularly with Z-scheme photocatalysts. As a prove of concept, S-scheme
765 heterostructures was reported as a better replacement because of its unambiguous
766 charge transfer mechanism. In addition, the review demonstrates the role of

767 functionalizing different photocatalysts platforms with co-catalyst for effective CO₂
768 adsorption, suppression of photogenerated electron-hole pairs, efficient light absorption
769 etc. The literature also emphasizes the importance of theoretical investigations that can,
770 at least partially, explain the electron-transfer process that takes place in such
771 composites or hybrid systems, offering a logical strategy for future performance
772 enhancements based on the optimization of MOFs, metal complexes, semiconductors
773 and their hybrids.

774 Despite the success recorded so far in the field of photocatalytic CO₂ conversion to
775 solar fuel production using metal complex, metal oxides, Z-scheme, organic
776 semiconductors and MOFs, there is still a long way to go before having the scientific
777 and technological capability to make this “artificial photosynthesis” practical to use for
778 the production of hydrocarbon fuels and feedstock chemicals in large scale because of
779 the unsatisfactory light harvesting, low-conversion efficiency, and lack of specific
780 product selectivity. To begin with, developing more active and selective photocatalysts
781 capable of successfully retarding charge recombination and capturing the solar
782 spectrum is critical in the field of CO₂ photoreduction.

783 Another significant challenge in the field of CO₂ photoreduction is the lack of a
784 standard technique for measuring photocatalytic performance, as well as a relevant
785 parameter that allows quantitative comparison of CO₂ conversion efficiencies to
786 specific fuels. One of the reasons is that the final activity and selectivity of CO₂
787 conversion are influenced by a variety of conditions such as light intensity and
788 spectrum, reaction temperature, humidity, CO₂ concentration, pH and components of
789 the photoreaction solution, mass and distribution of photocatalysts, and even reaction
790 vessel shape. To correct this shortcoming and offer a solid foundation for further CO₂
791 conversion development, suitable performance evaluation systems for photocatalytic
792 CO₂ conversion are required. A major issue that should not be overlooked in this field
793 is confirming that CO₂ is the actual substrate for carbon-containing compounds, as
794 state-of-the-art CO₂ photoreduction activities are currently quite low. One way to
795 address this problem is to conduct trace experiments in order to confirm the carbon
796 source.

797 Ultimately, a better understanding of photocatalytic CO₂ conversion reaction and
798 deactivation mechanisms is required for optimizing surface, facets, phases, and other

799 material qualities, reaction circumstances, and other previously unknown features. It is
800 general knowledge in the scientific community that photocatalytic CO₂ conversions to
801 solar fuels are typically complex multielectron processes aided by H₂O, and the activity
802 and selectivity of specific products compete with those of other products. A
803 combination of experimental and theoretical findings from fundamental investigations
804 and computer simulations should be favored since it is the most effective way to
805 increase our understanding of CO₂ photoreduction mechanisms. In summary,
806 photocatalytic CO₂ conversion to solar fuels is a technology that meets two goals with
807 one method, providing a package solution to present global warming and energy
808 demand by utilizing unlimited solar energy and increasing atmospheric CO₂. As a
809 result, in both theory and practice, the research and design of CO₂ photoreduction
810 systems with high stability, recyclability, nontoxicity, high efficiency, and wide
811 spectral response under sunlight irradiation is crucial. It is our hope that this review
812 work will channel a new path and concomitantly play an interesting role in this
813 important research field.

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820 **Conflicts of interest**

821 The authors declare no conflict of interest

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