Abstract: Rising levels of atmospheric carbon dioxide due to the burning and depletion of fossil fuels is continuously raising environmental concerns about global warming and the future of our energy supply. Renewable energy, especially better utilization of solar energy, is a promising method for CO₂ conversion and chemical storage. Research in the solar fuels area is focused on designing novel catalysts and developing new conversion pathways. In this review, we focus on the photocatalytic reduction of CO₂ primarily in its neutral pH species of carbonate to formate. The first two-electron photoproduct of carbon dioxide, a case for formate (or formic acid) is made in this review based on its value as; an important chemical feedstock, a hydrogen storage material, an intermediate to methanol, a high-octane fuel and broad application in fuel cells. This review focuses specifically on the following photocatalysts: semiconductors, phthalocyanines as photosensitizers and membrane devices and metal-organic frameworks.

Keywords: CO₂ reduction; formate; photocatalyst

1. Introduction

The sun provides 100,000 TW of energy in one hour that is enough to power the earth for one year, [1] but the energy needs to be storable and transportable (i.e., chemical fuel) because renewable energy sources generally provide an intermittent supply of energy [2]. In principle, all terrestrial energy sources, such as fossil fuels and uranium, can be considered as a solar fuel; it just depends on the time frame. For the purpose of this review, when solar energy is converted into chemical fuel on a diurnal basis the term solar fuels applies. As a mitigation strategy, C1 sources such as CO₂ or its pH neutral dissolved version, bicarbonate become concentrated energy sources for long-term storage capacity via energy input from solar irradiation [3]. In 2019, fossil fuels still supply 84% of the world’s energy [4]. In addition to limitations in the availability of fossil fuels, the emission of greenhouse gases, especially carbon dioxide, upon the combustion of fossil fuels is a major contributor to rising levels of anthropogenic carbon dioxide in the atmosphere. With the limitations in availability of fossil fuels, new sources of energy that provide a large-scale, sustainable energy supply must be developed. Solar energy is the most abundant renewable energy source available that can meet our future energy demands [5]. One potential approach towards generating renewable fuels is to use solar energy to directly reduce atmospheric or locally produced CO₂ to liquid fuels. This approach, referred to as “chemical carbon mitigation” can lead to methanol as an end product, a useful solar fuel. The concept of “the methanol economy,” championed by Chemistry Nobel laureate George Olah, highlights methanol as a renewable and readily transportable fuel and an alternative to the hydrogen economy. A key component to several C1 conversion methods in the methanol economy is
the solar-driven conversion of carbon dioxide to formic acid and ultimately to methanol, a renewable and regenerative C1 fuel [6–8].

The photocatalytic reduction of CO_2 is a multi-electron transfer process that can lead to the formation of many different products depending on the reaction pathway and the number of electrons transferred. Two-electron products include carbon monoxide, formic acid and oxalate. Methanol is the six-electron product and methane is the result of eight electron transfers [9–13]. The reduction half-reaction utilizes the photogenerated electrons, leaving behind the photogenerated holes. Ideally, the oxidation half-reaction would lead to the oxidation of water generating hydrogen or oxygen but very few systems can accomplish simultaneous oxidation and reduction reactions [9]. Therefore, research has focused on developing a sacrificial agent that can efficiently scavenge the photogenerated holes.

Photocatalysis follows three key steps (Figure 1): (1) Photon absorption by semiconductor, (2) charge separation, (3) surface reactions. Semiconductors are attractive materials for photocatalysis because their band gap energies are similar to that of UV or visible light (Figure 2) [9]. Upon absorption of a photon with energy greater or equal to the band gap of the semiconductor, an electron is excited from the valence band to the conduction band, leaving behind a hole. The photo-generated charge carriers then migrate to the semiconductor surface and transfer to the adsorbed molecules, which initiates the subsequent oxidation or reduction reactions. The formation of charge carriers is followed by several de-excitation pathways (Figure 1). Transfer of the charge carrier, either electron or hole, to the acceptor molecules leads to its oxidation or reduction (pathway 3 and 4). The carriers can recombine with the opposite charge carrier trapped at the surface (pathway 5) or recombination can occur in the bulk of the semiconductor (pathway 6). Three major drawbacks of photocatalysis include (1) narrow region of optical absorption, (2) rapid electron/hole recombination and (3) lack of understanding of photocatalysis mechanisms. This review aims to address these challenges.

**Figure 1.** Photo-excitation of a semiconductor and subsequent generation of charge carriers and decay pathways. X = electron donor, Y = electron acceptor.
Figure 2. Valence and conduction band edge potentials of various semiconductors, along with reduction potentials for CO₂/HCOOH, NAD⁺/NADH, H⁺/H₂ and H₂O/O₂.

This review is structured as follows: Sections 2 and 3 discusses the fundamentals of photocatalytic CO₂ reduction and explains why our work is focused on photocatalytic bicarbonate reduction to formate. Section 4 divides the catalysts into semiconductors, phthalocyanine-semiconductors and metal-organic frameworks. Lastly, Section 5 discusses the outlook of photochemical CO₂ reduction to formate and Section 6 summarizes the review with concluding remarks.

2. Fundamentals of Photocatalytic CO₂ Reduction

Thermodynamics of CO₂ Reduction

Photocatalytic reduction of CO₂ has a positive ΔG° value, meaning the process is non-spontaneous and requires significant energy input from the incident photons. As mentioned previously, methanol production from CO₂ reduction requires six protons and six electrons. Recently, there are studies in which homogeneous sensitizers coupled with metal co-catalysts have been shown to produce only CO and formic acid [14]. This observation of the incomplete six-electron reduction to methanol is governed by thermodynamics. Methanol production in an aqueous medium at pH 7 occurs at a slightly more positive potential (−0.39 V vs. NHE) than formate (−0.58 V vs. NHE) (Table 1). In addition, reduction of CO₂ to formate only requires two electrons whereas reduction to methanol requires six.

| Product          | Reaction                                      | E° (V vs. NHE) | Equation |
|------------------|-----------------------------------------------|----------------|----------|
| Hydrogen         | 2H₂O + 2e⁻ → 2OH⁻ + H₂                        | −0.41          | (1)      |
| Methane          | CO₂ + 8H⁺ + 8e⁻ → CH₄ + 2H₂O                  | −0.24          | (2)      |
| Carbon monoxide  | CO₂ + 2H⁺ + 2e⁻ → CO + H₂O                    | −0.51          | (3)      |
| Methanol         | CO₂ + 6H⁺ + 6e⁻ → CH₃OH + H₂O                 | −0.39          | (4)      |
| Formic acid      | CO₂ + 2H⁺ + 2e⁻ → HCOOH                      | −0.58          | (5)      |
| Ethane           | 2CO₂ + 14H⁺ + 14e⁻ → C₂H₆ + 4H₂O              | −0.27          | (6)      |
| Ethanol          | 2CO₂ + 12H⁺ + 12e⁻ → C₂H₅OH + 3H₂O            | −0.33          | (7)      |
| Oxalate          | 2CO₂ + 2H⁺ + 2e⁻ → H₂C₂O₄                    | −0.87          | (8)      |

Since carbon is in its highest oxidized state in CO₂, its reduction can lead to a wide variety of products (CO, CH₄, CH₃OH, HCOOH and many other products). CO₂ is a thermodynamically stable and chemically inert molecule with the C=O bond possessing a high dissociation energy of ~750 kJ/mol and C-C bond of ~336 kJ/mol, indicating a significant amount of energy input [16,17]. Moreover, the breaking of the C=O bonds and the bending of the molecular from linear to bent has
been shown to require a large input of energy [18]. In addition, Equation (9) has been shown to be the necessary step to activate CO₂, which has a very negative potential; therefore, high overpotential is needed to convert a CO₂ molecule to products [9,13].

\[
\text{CO}_2 + e^- \rightarrow \text{CO}_2^{--} \quad E^\circ = -1.90 \text{ V vs. NHE} \quad (9)
\]

We chose to highlight bicarbonate reduction in this study because of its reduction efficiency over dissolved CO₂ gas due to its limited solubility of CO₂ in water (0.033 M at 298 K and 1 atm) [19]. As several reports require the use of aqueous conditions, bubbled CO₂ poses a concentration disadvantage. In a previous study by our group [20], we questioned the standard assumption that CO₂ was the only species undergoing reduction even though numerous publications were using a bicarbonate buffer. This paper was among the first to conduct a control experiment with only bicarbonate buffer and no bubbled CO₂ [21,22]. From this control experiment, we discovered that bubbling CO₂ did not result in significantly higher formate production. Consequently, we decided to focus our efforts on bicarbonate reduction due to the following major issues with CO₂. First, a considerable practical problem with atmospheric capture is that the concentration of CO₂ in the air is still fairly low at 100’s of ppm [23]. While several concentrated CO₂ sources exist at fossil fuel burning plants or in some cases oil drilling activities, it is very hard to supply a reactor with enough CO₂ if it is being drawn from the atmosphere. Our experimental conditions parallel ocean bicarbonate concentration of 0.033 M [19] and with the continual acidification of the ocean due to dissolved carbon dioxide, it is relevant to capture bicarbonate and convert it to a value-added product.

3. The Case for Photons to Formate

In comparison to hydrogen, fuels based on carbon hold the advantage when it comes to denser volumetric energy along with transportation and storage within the current industrialized infrastructure. Converting CO₂ into value-added chemicals could contribute to negative emission technologies (NETs) by carbon sequestration into acetic acid, ethylene and formic acid instead of expensive geological storage [11]. Of these commodity chemicals, formate production and its growing chemical application has increased significantly over the past decade [24]. Furthermore, in relation to higher Cₙ homologs, CO₂ reduction to specialty chemicals in the range of C₁-C₃ such as formic acid production (0.2 MtC/yr) or propanol (0.1 MtC/yr) offers a brighter outlook for near term economic sustainability [25–27]. By comparison, carbon mitigation at the GtC/yr scale, which is ultimately impactful toward global climate change, will necessitate chemical conversion of greenhouse gases to be competitive with the production of fossil fuels such as coal (4 GtC/yr) and natural gas (1.4 GtC/yr) [28,29].

Techno-Economic Analysis

Even though CO₂ reduction is a widely studied field, much of the research is focused on the fundamental aspects of catalyst design and product selectivity. However, for this process to be commercialized, many requirements need to be met such as (1) continuous operation, (2) high product selectivity and throughput and (3) long-term stable operation [30]. In addition, it is essential that the energy used in the CO₂ conversion process does not generate additional CO₂. Recent studies on the economic feasibility of a commercial CO₂ reduction reactor show that formic acid is one of the only products that has potential to be made on a large-scale basis. Jouny et al. calculated the end-of-life net present value (NPV) of a CO₂ electrolyzer for the production of 100 tons/day of various CO₂ reduction products and found that only carbon monoxide and formic acid were the only economically viable products with NPVs of $13.5 million and $39.4 million, respectively [25]. Spurgeon and Kumar analyzed electrochemical conversion of flue gas CO₂ to liquid products and found that electrosynthesized formic acid from CO₂ was analyzed to be near market prices as a bulk chemical, even though it is not promising as an economic fuel. The major issue was the high capital cost for CO₂ electrolyzers since high Faradaic efficiency, high current densities and reduced electrolyzer
cost is necessary for economic viability [31]. Rumayor et al. carried out a techno-economic analysis of electrochemical reduction of CO\textsubscript{2} to formic acid and found that it is not yet profitable and competitive under current market conditions due to the high production costs [32].

4. Photocatalytic CO\textsubscript{2} Reduction to Formic Acid

4.1. Semiconductors

Halmann and Inoue were the first to reduce CO\textsubscript{2} with semiconductor photocatalysts. Within a year of each other, both published their works in *Nature* reported the photo-reduction of CO\textsubscript{2} in aqueous medium. In 1978, Halmann constructed a photoelectrode consisting of p-type gallium phosphide that produced formic acid after 18 h of irradiation [33]. A year later, Inoue reported the reduction of CO\textsubscript{2} using several photosensitive semiconductor powders (TiO\textsubscript{2}, ZnO, CdS, GaP, SiC and WO\textsubscript{3}) suspended in water [34]. Inoue’s work was one of the first studies to hypothesize that for photocatalysis to be efficient, photo-excited electrons in the more negative conduction band have greater ability to reduce carbon dioxide. Even though this work produced low quantum yields (0.0005%), it was an important early study that inspired many other researchers. Following these two papers, both authors continued to make novel discoveries in this field. Halmann, in 1982, demonstrated enhanced formate production could be achieved by using oxides of rare earth dopants (Eu\textsubscript{2}O\textsubscript{3}, Sm\textsubscript{2}O\textsubscript{3}, Nd\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}) to dope large band gap semiconductors (BaTiO\textsubscript{3}, LiNbO\textsubscript{3}) [35]. The optical properties of the catalysts were studied by diffuse reflectance spectroscopy, which uncovered the fact that rare earth dopants allowed the extension of optical absorption in the visible region of approximately 600 nm. A year later, Halmann reported the photoelectrochemical reduction of aqueous CO\textsubscript{2} using a single crystal p-gallium phosphide and p-gallium arsenide as photocathodes in neutral or weakly acidic medium [36]. The main product was determined to be formate (71 \(\mu\)mol) but formaldehyde and methanol were also produced. The influence of pH on the behavior of the electrodes was studied and a strong photo-effect was seen for all pH values. The next year, Halmann once again studied TiO\textsubscript{2} in the photo-reduction of CO\textsubscript{2}, this time doped with RuO\textsubscript{2} [37]. They found that by doping anatase TiO\textsubscript{2} with RuO\textsubscript{2}, formate was the predominant product and efficiency reached 0.04%. Later in 1995, Inoue reported on the photoreduction of CO\textsubscript{2} using chalcogenide semiconductor microcrystals. This study synthesized cadmium-loaded ZnS microcrystals in a sodium bicarbonate buffer and bubbled CO\textsubscript{2}, which produced the highest quantum efficiency of 32.5%, twice as large as that obtained on bare ZnS microcrystals. However, the quantum efficiency was determined using 280 nm irradiation, which would explain the high efficiency by using monochromatic light. 2-propanol was used as a hole scavenger and it was found that Cd loading was an important factor in formate production. It was also reported that with increasing mole fraction of Cd, formate production actually decreased and that the optimal Cd loading is 0.5–0.67%. Other metals such as Pb, Ni, Ag and Cu were used but none produced as high efficiency as Cd-ZnS [38].

Since the work by Inoue, ZnS has become an attractive semiconductor photocatalyst because of its non-toxic and earth abundant attributes and its effectiveness in the reduction of CO\textsubscript{2}. Kanemoto was able to achieve sufficient formate production of 75.1 \(\mu\)mol/h but this experiment was performed at 313 nm irradiation [39]. These findings also confirmed 2-propanol to be the most efficient electron donor amid sodium phosphate, sodium sulfate and triethanolamine. Johne and Kisch loaded ZnS onto large surface area SiO\textsubscript{2} particles to produce formate under UV irradiation. Later, 2,5-dihydrofuran was used as a reducing agent, which assisted in the production of 7000 \(\mu\)mol of formate [40].

Our group recently explored the photoreduction of bicarbonate to formate using wurtzite and sphalerite ZnS particles [20]. ZnS was studied in depth under the parameters of size, crystal lattice, surface area and band gap on the productivity of formate. Photochemical experiments were performed under air mass coefficient (AM 1.5 and 0) solar simulator conditions. Formate production was negligible under AM 1.5 conditions but significantly increased under AM 0 conditions due to the inclusion of shorter wavelength photons. This work was one of the first to question the standard assumption that CO\textsubscript{2} is the only species undergoing reduction. Compared to earlier works reporting bubbled CO\textsubscript{2} in the
presence of bicarbonate, this work suggests that bicarbonate was the predominant species undergoing reduction. As the C-H bond undergoes oxidation in 2-propanol, glycerol with three hydroxyllic positive hole scavengers was hypothesized as an improved semiconductor hole-scavenger and green chemistry solvent glycerol greatly improved the efficiency of the reaction. Continuing with ZnS, our group studied copper (I) oxide (Cu$_2$O) in the photoreduction of bicarbonate to formate. This work examined micron- and nano-particulate Cu$_2$O and synthesized a Ag/Cu$_2$O nanocomposite [41]. Due to plasmon-induced electron transfer from silver to Cu$_2$O, an enhanced formate production was found with the Ag/Cu$_2$O nanocomposite photocatalyst at 5.5% apparent quantum efficiency (Figure 3). In addition, an Au/TiO$_2$ and Ag/TiO$_2$ nanocomposite photocatalyst could reach apparent quantum efficiencies of 2.4% and 7.8%, respectively [42,43]. Beierle et al. designed a titanium nitride-titanium dioxide nanocomposite for bicarbonate reduction to formate. This work demonstrated that under solar illumination, the TiN-TiO$_2$ nanocomposite has higher photocatalytic activity than bare TiN or TiO$_2$, this nanocomposite can also greatly enhance formate production and remain stable for 8 h [44].

Baran et al. synthesized nanocrystalline zinc sulfide surface-modified with ruthenium(0) for the photocatalytic CO$_2$ reduction to formate, carbon monoxide and methane [45]. Formation of acetone was also observed due to the oxidation of the hole scavenger isopropanol. Surface-modified ZnS was more efficient than pure ZnS due to (1) the lowering of the CO$_2$ activation energy, (2) collection of electrons

Figure 3. Proposed mechanism for (a) Cu$_2$O semiconductor and (b) Ag/Cu$_2$O (blue block arrow represents resonant energy transfer from metal to semiconductor). Reproduced from [41], with permission from American Chemical Society, 2018.
at Ru particles resulted in a better charge separation and (3) better CO\textsubscript{2} desorption at the surface of modified ZnS. Both polar and non-polar solvents were tested and it was reported that in a polar solvent (water), formate is the major product and water was a better H-transfer agent than isopropanol. Kuwabata et al. employed ZnS microcrystallites for photocatalytic CO\textsubscript{2} reduction to methanol and formate by using methanol dehydrogenase and (MDH) and pyrroloquinoline quinone (PQQ) as an electron mediator for MDH and 2-propanol as a positive hole scavenger [46]. Acetone production resulting from the oxidation of 2-propanol was also studied.

Irvine et al. used CdS, ZnO, SiC, BaTiO\textsubscript{3} and SrTiO\textsubscript{3} to photochemically reduce aqueous CO\textsubscript{2} [47]. Product analysis showed the formation of formate, formaldehyde and methanol; the highest efficiency was obtained with ZnO, CdS and SiC. Continuing on Irvine’s work, Eggins et al. used CdS or ZnS colloids for the photo-reduction of CO\textsubscript{2} to produce formate and other dimeric and tetrameric products such as oxalate, glyoxylate, glycolate and tartrate. Other semiconductors studied included ZnO, SiC, BaTiO\textsubscript{3} and SrTiO\textsubscript{3} [48]. This work discusses the role of several hole acceptor (or electron donor) compounds that assist in reacting with photogenerated holes. Different electron donors tested include iron ferricyanide, hydroquinone, 2-propanol, RuO\textsubscript{2} and hypophosphite. This paper highlights that semiconductors with the most negative conduction band potential results in the best quantum yields because they have a stronger reducing potential. This work concluded that ZnS resulted in the highest quantum yield among all the semiconductors tested. Henglein et al. reported the efficient photoreduction of CO\textsubscript{2} to formic acid using SiO\textsubscript{2}-stabilized ZnS and 2-propanol as electron donor. By employing this system 0.80% AQE was achieved [49].

Kaneco and coworkers published three studies, all employing TiO\textsubscript{2} in a liquid CO\textsubscript{2} medium [50–52]. In the first effort, the effect of temperature, pressure, illumination time and surface area were examined. It was found that the formate yield was neither affected by temperature nor pressure. Formate production increased sharply with illumination time up until 5 h and progressed slowly until 30 h. A similar trend was observed with the surface area of the catalyst, formate increased linearly with increasing surface area of TiO\textsubscript{2} up to 0.4 m\textsuperscript{2}/g. Electron spin resonance elucidated the reaction mechanism of the reaction, which identified two radical species, photogenerated Ti\textsuperscript{3+} and CO\textsubscript{2}•− radical anion which resulted from the first electron transfer to CO\textsubscript{2}. In their follow-up work, Kaneco and coworkers continued to investigate the photoreduction of high-pressure CO\textsubscript{2} using TiO\textsubscript{2} powders with 2-propanol as a positive hole scavenger [51]. Methane was found to be the main reduction product; formate was also detected but only under extremely high pressures of CO\textsubscript{2}. In 1999, Kaneco and coworkers continued to study TiO\textsubscript{2} powders in supercritical fluid CO\textsubscript{2} by the investigation on the effects of temperature, pressure, irradiation time, surface area and aqueous solution for protonation. This study determined that formate production increased with an acidic pH medium because H\textsuperscript{+} are advantageous for desorption of reaction intermediates from the surface of TiO\textsubscript{2} [52]. These two works were the first to point out that photo-excited TiO\textsubscript{2} results in (Ti\textsuperscript{3+}–O•\textsuperscript{-})\textsuperscript{-} species (Figure 4) [51,52].

Liu et al. studied photocatalytic CO\textsubscript{2} reduction on CdS particles with and without surface modification in various solvents [53]. Formate and carbon monoxide were the two major products, as well as acetone from the oxidation of 2-propanol. The type of solvent and surface modification played a major role in the selectivity of the products. The reduction of CO\textsubscript{2} in acetonitrile produced carbon monoxide and formate, while in dichloromethane produced carbon monoxide only. Kisch reported CdS supported on silica and zinc sulfide to photocatalyze the reduction of bicarbonate to formate [54]. For CdS supported on zinc sulfide, it was found that the optimal CdS loading was 5%, which increased formate production 40-fold and 16-fold as compared to bare CdS and ZnS. Formate production was found to be dependent on bicarbonate concentration, when bicarbonate concentration increased from 33 to 60 mM formate production was enhanced by 10%. Formate production decreased by 20% when the pH was lowered to 5.3 but at a pH of 11.2, formate production increased by 25%. Zhang et al. used manganese sulfide (MnS) to reduce bicarbonate to formate at neutral pH [55]. Both ZnS and MnS have their conduction bands at highly reducing positions at −1.04 and −1.19 V versus NHE. This work
results in quantum efficiency of 4.2%, however, the wavelengths utilized fell within the UV region of the solar spectrum, between 200 and 400 nm.

![Figure 4](image-url)

Figure 4. Proposed mechanism of photocatalytic reduction of high-pressure CO₂ using TiO₂ and 2-propanol as a hole scavenger. Reproduced from [51], with permission from Elsevier, 1998.

Xia et al. synthesized a multi-walled carbon nanotube (MWCNT) supported TiO₂ and found that the addition of MWCNT greatly enhanced the photocatalytic activity of TiO₂ (Figure 5) [56]. As with other doped catalysts, it was found that there is an optimal amount of MWCNT before it begins to decrease the photocatalytic activity of TiO₂ due to the fact that excessive MWCNT can shield the TiO₂ from absorbing UV light. The optimal amount of MWCNT prevents TiO₂ from aggregating and can delay electron/hole recombination. Qin et al. made a bifunctionalized TiO₂ film containing a dye-sensitized zone and a catalysis zone designed for visible light photocatalytic CO₂ reduction (Figure 6) [57]. Electrons transferred from the dye to the conduction band of TiO₂ resulted in highly efficient conversion of CO₂ to formate, formaldehyde and methanol. After the electron injection, the dye is oxidized to dye⁺, which can be regenerated by accepting electrons from I⁻ from the electrolyte. Ulagappan et al. studied the photoreduction of gaseous CO₂ in Ti-silicate molecular sieves using methanol as an electron donor [58]. The main result of the study is the detection of formate and it was proposed that upon excitation of the metal center, transient Ti⁺⁺ reduces CO₂ while methanol is oxidized.

![Figure 5](image-url)

Figure 5. Photocatalytic CO₂ reduction to CH₄, HCOOH and C₂H₅OH using TiO₂-decorated multi-walled carbon nanotube (MWCNT).
In the 2000s, doping, co-catalyst and extending optical absorption to the visible region became a popular area for research. Sato et al. coupled a p-type semiconductor (N-doped Ta$_2$O$_5$) with a ruthenium complex as an electrocatalyst to produce formate from CO$_2$ [59]. This was the first report of electron transfer from semiconductor in the excited state to a metal complex in the ground state. Triethanolamine (TEOA) was used as an electron donor as well as a proton source and the measured quantum yield was 1.9% at 405 nm. A year later, Sato et al. studied the photoelectrochemical reduction of CO$_2$ over p-type InP/Ru complex polymer hybrid photocatalyst [60]. This reduction, using H$_2$O as an electron donor and proton source was achieved by using a two-step excitation process called a Z-scheme (Figure 7). Highly selective CO$_2$ photo-reduction was achieved by Arai and coworkers by combining Cu$_2$ZnSnS$_4$ (CZTS) with a metal complex electrocatalyst [61]. The main product was identified to be formate, which demonstrates the selectivity and efficiency of the hybrid semiconductor-metal-complex-electrocatalyst catalyst. Suzuki et al. continued on that idea of p-type photoactive N-doped Ti$_2$O$_5$ with a ruthenium complex, which can efficiently reduce CO$_2$ to formate using visible light [62].

Co-catalysts became a popular method to enhance semiconductor efficiency. Iizuka et al. used Ag as a co-catalyst for ALa$_4$Ti$_4$O$_{15}$ (where A = Ca, Sr and Ba) to reduce CO$_2$ to formate [63]. No sacrificial agent was used because water was consumed as a reducing agent (electron donor). It was found that the optimum Ag loading was 2 wt% and that BaLa$_4$Ti$_4$O$_{15}$ was the most active photocatalyst. Palladium is another noble metal that is often used as a co-catalyst. Raja et al. synthesized two photocatalysts-anodized titanium oxide nanotubes (T-NT) and bismuth titanate (BTO) decorated with palladium nanoparticles [64]. Pd-BTO showed a 2-fold increase in formic acid (110 µmol/h/g) yield when compared to bare BTO or T-NT, which is attributed to better charge separation in the hybrid Pd-BTO and the higher visible light harvesting ability of BTO because of its lower bandgap.
Figure 7. Illustration of the Z-scheme for CO$_2$ reduction. Reproduced from [60], with permission from American Chemical Society, 2011.

Mendoza et al. employed Co$_3$O$_4$ powders for CO$_2$ photo-reduction under visible light irradiation [65]. Co$_3$O$_4$ is a p-type semiconductor with band gap of 2.0 eV and has a conduction band edge that is more negative than the potentials of the CO$_2$ reduction reactions. In this study, formate was produced without any hole scavenger nor photo-sensitizer. Qin et al. synthesized a bismuth yttrium oxide (BiYO$_3$) photocatalyst for CO$_2$ reduction to formate under visible light irradiation [66]. Due to its large surface area and smaller band gap, BiYO$_3$ produced fewer hydroxyl radicals to give a higher formate yield.

Most recently, copper oxide and copper oxide-derivatives have been gaining attention as a highly active and earth abundant photocatalyst. Ali and coworkers designed a Z-scheme heterostructure composed of reduced titania and Cu$_2$O capable of reducing CO$_2$ to CH$_4$. Due to the Z-scheme architecture, Cu$_2$O was protected against photocorrosion and the photocatalyst was stable for 42 h. In addition, the synergistic interactions between reduced titania and Cu$_2$O resulted in 0.13% photoreduction of CO$_2$ to CH$_4$ [67]. Yin et al. grafted copper oxide nanoclusters onto niobate nanosheets, which served as a light harvesting component. This work found that photogenerated holes in the valence band of niobate nanosheets react with water and photogenerated electrons in the conduction band is injected into the copper oxide nanoclusters resulting in the production of carbon monoxide [68]. Lan et al. loaded Cu nanoparticles onto TiO$_2$ which exhibited significantly higher photocatalytic activity than pure TiO$_2$ for CO$_2$ reduction and selective for carbon monoxide [69]. Bae et al. synthesized zinc oxide-copper (I) oxide hybrid nanoparticles in colloidal forms with copper (I) oxide nanocubes bound to zinc oxide. This photocatalyst exhibited high selectivity for methane (>99%) which was attributed to the optimal band alignment of zinc oxide and copper (I) oxide, surface defects, high surface area and colloidal morphology of the catalyst [70]. Nogueira et al. evaluated the effect of electrolyte on photochemical CO$_2$ reduction using CuO nanoparticles and found electrolyte strongly influences product selectivity. NaOH led to methane production while Na$_2$C$_2$O$_4$ led to oxygen production [71]. Dedong et al. synthesized a Cu$_2$O/coal-based carbon nanoparticle hybrid to reduce CO$_2$ to methanol [72]. Zhang et al. fabricated an Ag-Cu$_2$O/ZnO nanorod hybrid catalyst and found Cu$_2$O enhances the CO$_2$ chemisorption on the catalyst surface while the formation of Z-scheme system between Cu$_2$O and ZnO facilitates charge separation. Silver nanoparticles onto Cu$_2$O leads to higher photocatalytic activity due to electron transfer from silver to Cu$_2$O [73]. Aguirre et al. found that TiO$_2$ can protect Cu$_2$O from undergoing photocorrosion when a Cu$_2$O/TiO$_2$ hybrid catalyst is formed. This hybrid creates an efficient Z-scheme which facilitates electron transfer from TiO$_2$ to Cu$_2$O [74]. Park et al. synthesized both CuO-TiO$_2$ and Cu$_2$O-TiO$_2$ and demonstrated this hybrid catalyst has enhanced light absorption and rapid charge
separation due to the intrinsic p-n heterojunction of the material, leading to improved photocatalytic activity [75]. Gusain et al. prepared reduced graphene oxide-copper oxide nanocomposites by covalent grafting of CuO nanorods onto reduced graphene oxide. Bare CuO showed low photocatalytic activity due to rapid charge carrier recombination but rGO-CuO and rGO-CuO showed significantly higher photocatalytic activity in the reduction of CO₂ to methanol under visible light irradiation [76]. Zhai et al. synthesized a core-shell structure containing two co-catalysts capable of reducing CO₂ to methane and carbon monoxide. They propose that the CuO shell provides sites for CO₂ reduction while the Pt core extracts photogenerated electrons from TiO₂ [77]. Wu et al. observed that the (110) facet of a single CuO particle is capable of reducing CO₂ to methanol while the (100) facet is inert. The oxidation state of the active sites changes from Cu(I) to Cu(II) due to CO₂ and H₂O adsorption and changes back to Cu(I) after CO₂ conversion under visible light irradiation [78]. Table 2 summarizes the different types of semiconductors used in photocatalytic CO₂/bicarbonate reduction to formate and other products.

**Table 2. Summary of CO₂ reduction using semiconductors.**

| Light Source | Reaction Medium and Electrolyte | Catalyst | Formate & Other Products | Ref. |
|--------------|--------------------------------|----------|--------------------------|------|
| Halogen lamp at 365 nm | Electrode consisting of single crystal GaP in 0.05 M K₂HPO₄/KH₂PO₄ | GaP | HCOOH: 1.2 × 10⁻² M HCHO: 3.2 × 10⁻⁴ M CH₃OH: 1.1 × 10⁻⁶ M | [33] |
| 500 W Xe lamp | Aqueous Suspension of semiconductor in water | TiO₂, ZnO, CdS, GaP, SiC, WO₃ | HCOOH: 1.8 × 10⁻³ M CH₃OH: 14.6 × 10⁻⁴ M ZnO: HCOOH: 1.2 × 10⁻³ M CH₃OH: 3.5 × 10⁻⁴ M CdS: HCOOH: 2.0 × 10⁻³ M CH₃OH: 11.7 × 10⁻⁴ M GaP: HCOOH: 1.0 × 10⁻³ M CH₃OH: 11.0 × 10⁻⁴ M SiC: HCOOH: 1.0 × 10⁻³ M CH₃OH: 53.5 × 10⁻⁴ M WO₃: HCOOH: 0 CH₃OH: 0 | [34] |
| High pressure Hg lamp | Aqueous suspensions | Doped BaTiO₃, LiNbO₃ | HCOOH and HCHO | [35] |
| 150 W Xe lamp | Electrodes in 0.5 M Na₂CO₃ | Single crystal p-GaP, p-GaAs | p-GaP: HCOOH: 670 µmol HCHO: 13 µmol CH₃OH: 10 µmol p-GaAs: HCOOH: 320 µmol HCHO: 5 µmol | [36] |
| High pressure Hg lamp | Aqueous suspension in water | RuO₂-doped TiO₂ | HCOOH: 1.46 µmol/h HCHO: 0.18 µmol/h CH₃OH: 0.2 µmol/h | [37] |
| High pressure Hg lamp | Aqueous suspension in 1.5 × 10⁻³ M NaHCO₃ | Cd-loaded ZnS | Quantum efficiency: HCOOH: 32.5% HCHO: 42.0% H₂: 5.0% | [38] |
| High pressure Hg lamp | Colloidal suspension in 0.7 M NaH₂PO₄ | ZnS | HCOOH: 75.1 µmol/h CO: 2.7 µmol/h H₂: 86.0 µmol/h | [39] |
| Tungsten-halogen lamp (λ > 350 nm) | Aqueous suspension in water | ZnS-loaded SiO₂ | HCOOH: 10 mmol | [40] |
| 1000 W Xe arc lamp | Aqueous suspension in 0.2 M NaHCO₃ | ZnS | HCOOH: 140 mmol formate/g cat-hr | [20] |
| 1000 W Xe arc lamp | Aqueous suspension in 0.2 M NaHCO₃ | Cu₂O | HCOOH: 2.78 mmol formate/g cat-hr | [41] |
| 1000 W Xe arc lamp | Aqueous suspension in 0.2 M NaHCO₃ | Au/TiO₂ | HCOOH: 55 mmol formate/g cat-hr | [42] |
| 1000 W Xe arc lamp | Aqueous suspension in 0.2 M NaHCO₃ | Ag/TiO₂ | HCOOH: 3.89 mmol formate/g cat-hr | [43] |
| 1000 W Xe arc lamp | Aqueous suspension in 0.2 M NaHCO₃ | TiN/TiO₂ | HCOOH: 3000 mmol formate/g cat-hr | [44] |
| Light Source | Reaction Medium and Electrolyte | Catalyst | Formate & Other Products | Ref. |
|-------------|---------------------------------|----------|--------------------------|------|
| 150 W XBO arc lamp | Aqueous suspension in water | Ru nanoparticles-loaded ZnS | HCOOH: 0.006 M | [45] |
| High pressure Hg lamp | Colloidal suspension in H3PO4 | ZnS microcrystalline | HCOOH: 11.6 µmol HCHO: 11.8 µmol CH3OH: 1.2 µmol | [46] |
| Medium pressure mercury lamp | Aqueous suspension in water | CdS, ZnO, SiC, Ba TiO3, SrTiO3 | HCOOH, HCHO | [47] |
| Medium pressure mercury lamp | Aqueous suspension in water | CdS, ZnS | ZnS: HCOOH: 320 µmol/L CdS: HCOOH: 87 µmol/L | [48] |
| Medium pressure mercury lamp | Aqueous suspension in water | SiO2-stabilized ZnS | HCOOH: 0.8% AQE | [49] |
| Medium pressure mercury lamp | Aqueous suspension in water | TiO2 | HCOOH: 8 × 10^-8 mol/g-cat | [50] |
| Xe lamp | Aqueous suspension in water | TiO2 | HCOOH: 2.3 × 10^-6 mol/g-cat CH4: 1.2 × 10^-6 mol/g-cat | [51] |
| 990 W Xe lamp | Power in supercritical fluid CO2 | TiO2 | HCOOH: 9 × 10^-6 mol/g-cat | [52] |
| 500 W high pressure mercury arc lamp | Aqueous suspension in water and 2-propanol | CdS | HCOOH: 0.4 µmol HCHO: 1.9 µmol CO: 0.6 µmol H2: 0.5 µmol | [53] |
| 100 W tungsten halogen lamp, 150 W xenon lamp | Aqueous suspension in water | CdS-SiO2, CdS-ZnS | CdS-SiO2: HCOOH: 10 × 10^-5 M HCHO: 3.4 × 10^-5 M CdS-ZnS: HCOOH: 4.5 × 10^-5 M | [54] |
| 450 W medium pressure UV Hg arc lamp | Aqueous suspension in water and 7.2 mM NaHS and 2.5 mM NaHCO3 | MeS | HCOOH: 200 µM | [55] |
| 15 W UV lamp λ = 365 nm | Aqueous suspension in water | MWCNT-supported TiO2 | HCOOH: 125.1 µmol/g CH4: 73.33 µmol/g C2H6OH: 149.36 µmol/g | [56] |
| 300 W Xe lamp | Electrode in water adjusted to pH 4 | Dye-sensitized TiO2 film | HCOOH: 1.8 mmol/cm² HCHO: 1.4 mmol/cm² CH3OH: 1.9 mmol/cm² | [57] |
| Pulsed Nd:YAG laser at 10 Hz, λ = 266 nm | Methanol | Ti silicate molecular sieve | HCOOH, CO | [58] |
| Xe lamp | Aqueous suspension in MeCN/TEOA | N-doped Ta2O5 (N-Ta2O5), linked with electrocatalysts [Ru(dcbpy)(bpy)](CO)22+ or [Ru- (dcbpy)2(CO)2]2+ | HCOOH: 1.9% quantum yield | [59] |
| Solar simulator with AM 1.5 filter | Aqueous suspension in water and 10 mM NaHCO3 | InP/Ru complex polymer hybrid | HCOOH: 4.71 µmol/cm² | [60] |
| Xe light source | Aqueous suspension in water | Cu2ZnSnS4 | HCOOH: 0.22 mM | [61] |
| 500 W Xe lamp | Aqueous suspension in acetonitrile/triethanolamine | N-doped Ta2O5 with [Ru(dcbpy)2] (CO)22+ | HCOOH: 1.9 quantum efficiency | [62] |
| 400 W high-pressure mercury lamp | Aqueous suspension in water | Ag-loaded ALa4Ti4O15 (A = Ca, Sr, Ba) | BaLa4Ti4O15: HCOOH: 150 µmol | [63] |
### Table 2. Cont.

| Light Source | Reaction Medium and Electrolyte | Catalyst | Formate & Other Products | Ref. |
|--------------|---------------------------------|----------|-------------------------|------|
| 300 W solar simulator with AM 1.5 filter | Thin films submerged in 0.1 M H₂SO₄ | Anodized titanium oxide nanotubes (T-NT), Pd-decorated bismuth titanate (BTO) | HCOOH: 160 µmol/h-g | [64] |
| 21 W LED lamp, λ = 510 to 620 nm | Aqueous suspension in water | Co₃O₄ | HCOOH: 4.53 µmol/g-h, HCHO: 0.62 µmol/g-h | [65] |
| 300 W Xe lamp | Aqueous suspension in 0.25 M NaOH and 0.1 M Na₂SO₃ | BiYO₃ | HCOOH: 1.68 µmol/L | [66] |
| 100W solar simulator with AM 1.5 filter | CO₂ passing through solid photocatalyst | Reduced titania-Cu₃O | CH₄: 462 nmol/g | [67] |
| Xe–Hg lamp | Aqueous suspension in 0.5 M KHCO₃ | Cu(II)-grafted Nb₂O₅ nanosheets | CO: 1.5 µmol | [68] |
| 300 W Xe lamp | Aqueous suspension in water | Cu₂O | CO: 244 µmol/g-h | [69] |
| 300 W Xe lamp | Aqueous suspension in 0.2 M Na₂CO₃ | ZnO-Cu₃O nanoparticles | CH₄: 1080 µmol/g-cat h, CO: 1.4 µmol/g-cat h | [70] |
| 5 W UVC lamp | Aqueous suspension in 0.1 M Na₂CO₃ | CuO | CH₄: 100 µmol/L-g, CO: 6 µmol/L-g | [71] |
| 300 W Xenon lamp | Aqueous suspension in 1M NaOH | Cu₂O/CNPs | CH₃OH: 236.4 µmol g⁻¹cat | [72] |
| 300 W Xe arc lamp | Aqueous suspension in water | Ag-Cu₂O/ZnO nanoparticles | CH₄: 9.94 µmol/g | [73] |
| 1 kW high-pressure Hg (Xe) arc lamp | Aqueous suspension in water | Cu₂O/TiO₂ | CH₄: 2.11 µmol g⁻¹cat h⁻¹ | [74] |
| 100 W Xenon solar simulator with AM 1.5 filter | Powder photocatalyst with CO₂ | Cu₂O-TiO₂ | CH₄: 221.6 ppm g-h | [75] |
| 20 W white cold LED flood light | Aqueous suspension in DMF and water | rGO-Cu₂O, rGO-CuO | CH₃OH: 1228 µmol/g, CH₃OH: 862 µmol/g | [76] |
| 200 W Xe lamp | Powder photocatalyst with CO₂ | TiO₂-loaded Pt and Cu | CH₄: 11 µmol/g-h, CH₄: 8.7 µmol/g-h, CH₄: 9.8 µmol/g-h | [77] |
| 300 W Xe lamp | Aqueous suspension in water | Cu₂O | CH₃OH: 1.2 mol g⁻¹ h⁻¹ | [78] |

### 4.2. Phthalocyanine-Semiconductor Composites

Phthalocyanines are macrocyclic heterostructures with aromatic conjugated complexes consisting of nitrogen and carbon atoms. They offer enormous potential as the light harvesting components of dye-sensitized semiconductors [79]. They also offer high photo and thermal stability and low toxicity. In addition, the close position of the TiO₂ conduction band with respect to the LUMO orbital energy of the phthalocyanines favors efficient charge transfer. When the phthalocyanines molecule is excited by visible light, electrons are excited from the HOMO to the LUMO energy level and is then injected into the conduction band of TiO₂.

In 1997, Premkumar et al. was able to produce formate from carbon dioxide upon photo-reduction by metal phthalocyanines (cobalt and zinc) adsorbed onto a Nafion membrane that acted as a...
photocatalyst in acidic aqueous solution containing triethanolamine as a hole scavenger [80,81]. The catalyst was immobilized in the Nafion membrane and because they are physically separated from the solution phase they are able to exhibit high photocatalytic efficiency (Figure 8). It was found that the membranes behave as a p-type semiconductor and high turnover numbers were achieved. In 2009, Liu et al. synthesized CoPc-loaded TiO₂ and in the presence of NaOH, produced high formate yield [82]. Na₂SO₃ was used as a hole scavenger and under optimal conditions, 1032 μmol/g cat of formate was produced. It was found that with the addition of CoPc, formate production significantly increased, with optimal CoPc loading being 0.5 wt%. The contact of TiO₂ and CoPc involves redistribution of charge. Because the oxidation potential of S₁ of CoPc is higher than the conduction band of TiO₂, while the energy of T₁ is lower than the conduction band of TiO₂ (Figure 9), it is thermodynamically feasible for electron transfer from CoPc to TiO₂. When this occurs, CoPc is oxidized to CoPc•+. The influence of NaOH, hole scavenger and irradiation time has been investigated. Because NaOH can dissolve more CO₂ than pure water, making HCO₃⁻ the predominant form in aqueous solution therefore accelerating the photoreduction [82]. The mechanism of CO₂ reduction with CoPc-loaded TiO₂ begins with photo-excitation of the CoPc from S₀ to S₁, which can subsequently transfer its electrons to the conduction band of TiO₂. CO₂ molecules adsorbed onto the surface of TiO₂ gain electrons and are reduced (Equations (10) and (11)) [81].

\[
\text{CoPc (S₀) + h} \nu \rightarrow \text{CoPc}^\ast (S₁) \quad (10)
\]

\[
\text{CoPc}^\ast (S₁) + \text{TiO}_2(\text{CB}) \rightarrow \text{CoPc}^{••} + \text{e}^\ast (\text{TiO}_2/\text{CB}) \quad (11)
\]

In 2009, Zhao et al. also synthesized a CoPc/TiO₂ nanocomposite to reduce CO₂ under visible light irradiation [83]. CoPc molecules are excited first and are able to inject their electrons into TiO₂, this allows for the increased separation of electron/hole pairs and thus increasing the photocatalytic efficiency to 1714 μmol/g cat. In 2013, Yazdanpour et al. synthesized copper phthalocyanine-modified TiO₂ (CuPc/TiO₂), which was coated on a stainless steel mesh and used for the photo-reduction of CO₂ in the presence of visible light [84]. Mele et al. synthesized copper and zinc phthalocyanine-loaded TiO₂ under visible light irradiation [79]. They reported that CuPc/TiO₂ was the most efficient yielding formate production of 208.5 μmol/g cat. In 2015, Mele expanded on their work of CuPc-loaded TiO₂ by studying both Cu(II) porphyrin and Cu(II) phthalocyanine loaded onto TiO₂ [85]. Cu(II) phthalocyanine-loaded TiO₂ was more efficient in the photoreduction of CO₂ to formate due to its favorable reduction potential. This work reported a detailed study of the effect of the amount of catalyst, initial pH, copper loading in the CuPc-TiO₂ composite, irradiation source and sensitizers. This work reported production values for formate of 239.5 μmol/g cat. Table 3 summarizes various phthalocyanine-enhanced semiconductors to reduce CO₂/bicarbonate to formate and other products.
Figure 8. Schematic illustration of the photocatalytic CO$_2$ reduction at MPC adsorbed in a Nafion membrane. (Circle represents the semiconducting nature of the adsorbed MPC Nafion membrane. MPC = CoPC or ZnPC, TEA = triethanolamine, CB = conduction band, VB = valence band and EF = Fermi level).

Figure 9. Photocatalytic CO$_2$ reduction using CoPc-loaded TiO$_2$. 
MOFs are superior to semiconductors because their light absorption ability can be easily tuned by organic linkers serving as antennas to activate the quantum dots [88]. Electron injections occur from the photo-excited organic linkers to the metal clusters, termed linker-to-cluster charge transfer (LCCT). MOFs are superior to semiconductors because their light absorption ability can be easily tuned.

### 4.3. Metal-Organic Frameworks

Metal-organic frameworks (MOFs) are a class of crystalline materials made by joining metal ions or clusters and organic linkers together. Inorganic metals are called secondary building units (SBU) and organic units are ditopic or polytopic organic carboxylates. The different combinations of organic and inorganic components, as well as varying the geometry, size and functionality has led to more than 20,000 different MOFs being synthesized [86]. The three most distinguishing features of MOFs are their large surface area and ultrahigh porosity; as well as its permanent porosity. MOFs are more than 20,000 different MOFs being synthesized [86]. Different MOFs are stable structures that do not collapse upon the removal of solvent. Compared to commercial TiO$_2$ (P-25) that have surface area of only 35–65 m$^2$/g, MOFs have a tremendous amount of surface area. Surface area of MOFs typically range from 1000 to 10,000 m$^2$/g and their porosity is greater than 50% of the MOF crystal volume [86]. MOFs are also shown to be thermally and chemically stable. It is these properties of MOFs that give them a great advantage over other porous materials such as zeolites and carbon-based materials.

Metal-organic frameworks (MOFs) are emerging as a new type of promising photocatalysts. MOFs are a class of crystalline and microporous material with a vast array of topologies and applications in numerous fields such as gas sensing, catalysis, gas storage and separation and drug delivery [87]. In MOFs the metal clusters can be regarded as inorganic semiconductor quantum dots that are linked by organic linkers serving as antennas to activate the quantum dots [88]. Electron injections occur from the photo-excited organic linkers to the metal clusters, termed linker-to-cluster charge transfer (LCCT). MOFs are superior to semiconductors because their light absorption ability can be easily tuned.

### Table 3. Summary of CO$_2$ reduction using phthalocyanines.

| Light Source | Reaction Medium and Electrolyte | Catalyst | Formate & Other Products | Ref. |
|--------------|---------------------------------|----------|--------------------------|------|
| 300 UV-VIS UV-VIS lamp and 400 W Xe-Halogen lamp S: SANOLUX HRC uv vis lamp 300 W H: RADIUM Xe-Halogen lamp 400 W | Aqueous suspension in water, pH adjusted by NaOH or H$_3$PO$_4$ | Lipophilic phthalocyanines TiO$_2$ composites | Product yield in μmol/g cat TiO$_2$ with pH 3 and a S/H light source: 131 HCOOH TiO$_2$-H$_3$Pc with pH 3 and a S/H light source: 75 HCOOH TiO$_2$-CuPc with pH 3 and a S/H light source: 208.5 HCOOH TiO$_2$-ZnPc with pH 3 and a S/H light source: 88.5 HCOOH TiO$_2$-CuPc with pH 7 and a S/H light source: 63.4 HCOOH TiO$_2$-CuPc with pH 13 and a S/H light source: 65.2 HCOOH TiO$_2$-CuPc with pH 3 and a S light source: 32.6 HCOOH TiO$_2$-CuPc with pH 3 and a H light source: 52.2 HCOOH | [79] |
| 500 W tungsten-halogen lamp | Membrane dipped in 0.1 M TEA and 0.1 M HClO$_4$ | MP-Nafion, MPC-Nafion | Ni/PP: 8 × 10$^{-5}$ mol Ni/CoTTP: 2.9 × 10$^{-4}$ mol Ni/FePC: 11 × 10$^{-4}$ mol Ni/ZnPc: 2 × 10$^{-4}$ mol | [80] |
| 500 W tungsten–halogen lamp | Membrane dipped in 0.1 M triethanolamine and 0.1 M HClO$_4$ | MPC-Nafion | Ni-CoPc: 1.7 × 10$^4$ mol Ni-ZnPc: 2.0 × 10$^4$ mol | [81] |
| 500 W tungsten–halogen lamp | Aqueous suspension in NaOH | CoPc-TiO$_2$ | With 0 [HCHO]/M and 0 [CH$_2$OH]/M: HCOOH: 289.9 μmol/(g cat) With 0 [HCHO]/M and 0.5 [CH$_2$OH]/M: HCOOH: 292.8 μmol/(g cat) With 0 [HCHO]/M and 5 [CH$_2$OH]/M: HCOOH: 301.1 μmol/(g cat) With 0.1 [HCHO]/M and 0 [CH$_2$OH]/M: HCOOH: 9731.3 μmol/(g cat) With 1 [HCHO]/M and 0 [CH$_2$OH]/M: HCOOH: 82662.5 μmol/(g cat) | [82] |
| 500 W tungsten-halogen lamp | Aqueous suspension in 0.1 N NaOH | CoPc-TiO$_2$ | 1.0 wt% CoPC/TiO$_2$: HCOOH: 450.6 μmol/g cat 0.7 wt% In-situ CoPC/TiO$_2$: HCOOH: 1487.6 μmol/g cat | [83] |
| 125 W high pressure mercury lamp | CO$_2$ passed through catalyst-coated reaction vessel | CuPc-TiO$_2$ | 14% photoconversion | [84] |
| 300 UV-VIS UV-VIS lamp and 400 W Xe-Halogen lamp | Aqueous suspension in water, pH adjusted by NaOH or H$_3$PO$_4$ | CuPc-TiO$_2$ | HCOOH: 239.5 μmol/g cat | [85] |
by modifications on the organic linkers to make them visible-light responsive [89]. Table 4 summarizes CO₂ reduction using various metal-organic frameworks.

**Table 4. Summary of CO₂ reduction using metal-organic frameworks.**

| Light Source | Reaction Medium and Electrolyte | Catalyst | Formate & Other Products | Ref. |
|--------------|--------------------------------|----------|--------------------------|------|
| 500 W Xe lamp | Aqueous suspension in 5:1 ratio of MeCN and TEOA | NH₂-Uio-66(Zr) | NH₂-Uio-66(Zr): HCOOH: 13.2 µmol in 10 h Mixed NH₂-Uio-66(Zr): HCOOH: 20.7 µmol in 10 h NH₂-Uio-66(Zr): HCOOH: None Mixed NH₂-Uio-66(Zr): HCOOH: 7.28 µmol | [88] |
| 300 W Xe lamp | Aqueous suspension in 5:1 ratio of MeCN and TEOA | MIL-101(Fe), MIL-53(Fe), MIL-88B(Fe), | NH₂-MIL-101(Fe): HCOOH: 178 µmol MIL-101(Fe): HCOOH: 59.0 µmol NH₂-MIL-53(Fe): HCOOH: 46.5 µmol MIL-53(Fe): HCOOH: 29.7 µmol NH₂-MIL-88(Fe): HCOOH: 30.0 µmol MIL-88(Fe): HCOOH: 9.0 µmol | [89] |
| 500 W Xe lamp | Aqueous suspension in 5:1 ratio of MeCN and TEOA | NH₂-MIL-125(Ti) | NH₂-MIL-125(Ti): HCOOH: 8.14 µmol NH₂-MIL-125(Ti) (λ > 450 nm): HCOOH: 3.83 µmol | [90] |
| 470 nm LED | Aqueous suspension in 4:1 ratio of DMF/TEOA solvent mixture containing 0.2 M 1-benzyl-1,4-dihydronicotiamide (BNAH) | Mn(bpydc)(CO)₃Br incorporated into Zr(IV)-based metal-organic framework | Turnover numbers for Products: Uio-67-Mn(bpy)(CO)₃Br(b) for 4 h: HCOOH: 50 Uio-67-Mn(bpy)(CO)₃Br(b) for 18 h: HCOOH: 110 | [91] |
| 300 W Xe arc lamp | Aqueous suspension in 4:1 mixed solution of acetonitrile (MeCN)-triethanolamine (TEOA), which contained 1-benzyl-1,4-dihydronicotiamide (0.1 M, BNAH) | Zr₄(μ₃-O)₂(C₆H₄O₂N₃)·17(C₆H₄O₂N₂)·0.83 | Zr₄(μ₃-O)₂(C₆H₄O₂N₃)·17(C₆H₄O₂N₂)·0.83: HCOOH: 31.57 µmol | [92] |

Fu et al. synthesized a Ti-based MOF Ti₆O₉(OH)₄(BDC)₆ (where BCD = benzene-1,4-dicarboxylate) and the photocatalytic reduction of CO₂ was performed in acetonitrile with triethanolamine (TEOA) as a sacrificial agent under visible light irradiation [90]. This MOF exhibited extremely high surface area of 1302 m²/g that produced 8.14 µmol of formate after 10 h. Upon irradiation in the LMCT band, a long-lived excited charge separate state occurs by transferring an electron from the organic ligand to Ti⁴⁺ (Figure 10). Sun et al. synthesized NH₂-Uio-66(Zr), which is a Zr-containing MOF composed of hexameric Zr₆O₇₂ units linked by benzenedicarboxylate (BDC) [88]. This study substituted the BDC ligand with 2-aminoterephthalic acid (ATA), which rendered the MOF visible-light responsive due to the amino substituent. In the presence of triethanolamine as a sacrificial agent, visible light irradiation was able to reduce CO₂ to formate reaching production values of 20.7 µmol/g cat-hr. Wang et al. reported synthesizing a series of earth-abundant Fe-containing MOFs that are able to reduce CO₂ under visible light irradiation [89]. The direct excitation of the Fe-O clusters induces the electron transfer from O²⁻ to Fe³⁺ to form Fe²⁺, which is responsible for the CO₂ reduction. In addition, when these MOFs are functionalized with an amine substituent, their catalytic efficiency is greatly increased. This is attributed to the existence of dual excitation pathways: excitation of the NH₂ functionality is followed by electron transfer to the Fe center and the direct excitation of Fe-O clusters. In the presence of TEOA as a sacrificial agent, formate production reached 178 µmol. Fei et al. incorporated a manganese bipyridine complex [Mn(bpydc)-(CO)₃Br] into a robust Zr(IV)-based MOF for CO₂ reduction to formate [91]. [Ru(dmb)₃]²⁺ was used as a photosensitizer and 1-benzyl-1,4-dihydronicotiamide (BNAH) was used as a sacrificial agent (Figure 11). The enhanced photocatalytic efficiency was ascribed to the structure of the framework providing isolated active sites, which stabilize the catalyst. The catalyst maintained its crystallinity and was reused over several runs. Most recently, Lee et al. synthesized a mixed metal (Zr/Ti) MOF to reduce CO₂ to formate under visible light irradiation [92]. TEOA was used as a sacrificial base and 1-benzyl-1,4-dihydronicotiamide (BNAH) as a sacrificial reductant. The MOFs...
were studied by photoluminescence spectroscopy to study charge transfer from organic linker to the metal cluster. This work resulted in high turnover numbers and the catalysts were recyclable over three runs.

**Figure 10.** Proposed mechanism for the photocatalytic CO\textsubscript{2} reduction using NH\textsubscript{2}-MIL-125(Ti) under visible light irradiation.

**Figure 11.** Proposed mechanism for photocatalytic formate production using UiO-67-Mn(bpy)(CO)\textsubscript{3}Br.

5. Future Perspectives and Outlook

The majority of this review is focused on semiconductors for CO\textsubscript{2}/bicarbonate reduction because they are the most widely used photocatalyst. However, quantum efficiencies are still low due to extremely rapid electron/hole recombination within the semiconductor, narrow optical absorption of the semiconductor, scattering of the semiconductor, competing hydrogen evolution reaction and products getting re-oxidized to CO\textsubscript{2}. Though these issues can be mitigated by using photosensitizers and hole scavengers, a lot of work still needs to be done to make the reaction more efficient. In addition, semiconductors eventually degrade over time, so more durable catalysts need to be designed. Plasmon-enhanced photocatalysis is a rapidly expanding field due to the excellent optical properties of plasmonic noble-metal nanoparticles such as Au and Ag. Plasmonic nanoparticles
primarily absorb in the visible region of the solar spectrum and are known to generate hot electrons that can be injected into the conduction band of semiconductors, allowing for excess electrons available for reduction. Plasmonic nanoparticles, along with organic dyes, can act as excellent photosensitizers for semiconductors.

Moving forward, design strategies for photocatalysts include the fabrication of three-dimensional hierarchical nanostructures to maximize surface area, catalyst kinks and defects and grain boundaries to allow for molecular adsorption to the catalyst surface. Different metal crystal structures and surface facets lead to different product distribution, therefore tuning the metal surface structure will allow for precise control over product selectivity. The addition of photosensitizers to render a catalyst visible light-responsive will maximize the region of optical absorption and the ability to utilize more of the solar spectrum. With these techniques, rational design of efficient, selective and durable catalysts is possible. With the development of these catalysts, one can then scale up and design reactors that can convert CO$_2$ or flue gas into value-added products.

6. Conclusions

In conclusion, many significant achievements have been made in the field of photocatalytic CO$_2$ reduction. In relation to hydrogen production, which remains an impactful renewable energy source, the case is made for the chemical conversion of CO$_2$ to formate in terms of near term economic feasibility and in juxtaposition to geological storage and sequestration. Based on this review, one can see that the majority of photocatalysts for CO$_2$ reduction to formate are comprised of semiconductors. However, due to their narrow region of optical absorption, many studies have incorporated ruthenium complexes, phthalocyanines, and employed metal-organic framework catalysts designed to be visible-light responsive. Other catalysts include the use of graphene and graphene oxide as electron sinks to improve charge separation. Albeit much effort has been put into studying CO$_2$ reduction, the photoconversion efficiency and selectivity for desired products is still low. The mechanism of CO$_2$ reduction still needs to be investigated in depth. The one-electron induced activation of CO$_2$ into the anion radical CO$_2$$^{•−}$ still requires a high overpotential, which seems to be the rate-limiting step. The development of photocatalytic materials for CO$_2$ reduction is rapidly expanding and will continue to reach higher efficiencies. As apparent quantum efficiencies improve with current research trends and new investigators entering the field, we assert that more practical device and design will become a major research component to the success of greenhouse gas mitigation and regenerative energy.

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