

# Photochemical and Photoelectrochemical Reduction of CO<sub>2</sub>

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## Keywords

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## Abstract

The recent literature on photochemical and photoelectrochemical reductions of CO<sub>2</sub> is reviewed. The different methods of achieving light absorption, electron-hole separation, and electrochemical reduction of CO<sub>2</sub> are considered. Energy gap matching for reduction of CO<sub>2</sub> to different products, including CO, formic acid, and methanol, is used to identify the most promising systems. Different approaches to lowering overpotentials and achieving high chemical selectivities by employing catalysts are described and compared.

## 1. INTRODUCTION

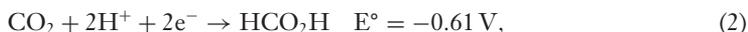
### 1.1. General Introduction

Research in the field of photochemical and photoelectrochemical reduction of CO<sub>2</sub> has grown rapidly in the last few decades. This growing research effort is a response by physical scientists and engineers to the increasing amount of CO<sub>2</sub> in the atmosphere and the steady growth in global fuel demand. This review presents much of the significant work done in this field over the past three decades. It then extends the discussion to a critical summary of previous work and prospects for future directions to develop catalytic systems that will reduce CO<sub>2</sub> with high efficiencies.

The catalytic conversion of CO<sub>2</sub> to liquid fuels is a critical goal that would positively impact the global carbon balance by recycling CO<sub>2</sub> into usable fuels. The challenges presented here are great, but the potential rewards are enormous. CO<sub>2</sub> is an extremely stable molecule generally produced by fossil fuel combustion and respiration. Returning CO<sub>2</sub> to a useful state by activation/reduction is a scientifically challenging problem, requiring appropriate catalysts and energy input. This poses several fundamental challenges in chemical catalysis, electrochemistry, photochemistry, and semiconductor physics and engineering.

### 1.2. The Difficulty of CO<sub>2</sub> Reduction

The thermodynamic potentials for various CO<sub>2</sub> reduction products can be seen in Equations 1–5 (pH 7 in aqueous solution versus a normal hydrogen electrode (NHE), 25°C, 1 atm gas pressure, and 1 M for other solutes) (1):



Although CO<sub>2</sub> has been shown to be reduced directly on metal surfaces, the overpotentials are either exceedingly high or the metal surfaces become poisoned and deactivated by the reduction products (2). In addition to thermodynamic considerations, there are also considerable kinetic challenges to the conversion of CO<sub>2</sub> to more complex products. Typically, multiple proton-coupled electron transfer (PCET) steps must be orchestrated with their own associated activation energies presenting kinetic barriers to the forward reaction. A great deal of success has been achieved in the reduction of CO<sub>2</sub> to CO and formate. However, the multiple electron and proton transfers necessary to produce more useful products such as methane or methanol have only been demonstrated with low efficiency. To achieve success at efficient production of a CO<sub>2</sub> reduction product that can serve as a liquid fuel directly (i.e., methanol) would be a considerable milestone for renewable energy and energy storage research.

### 1.3. Molecular Catalysts

To overcome the thermodynamic barriers of CO<sub>2</sub> reduction, molecular catalysts can be used to lower the overpotential by stabilizing the intermediate transition states between the linear CO<sub>2</sub> molecules and the intended product. CO<sub>2</sub> has multiple known binding modes to transition metal complexes (3). The metal can then act as an inner sphere electron transfer agent to activate CO<sub>2</sub> for

further transformation. With the choice of various metal centers and ligand structures, molecular catalysts are highly tunable to achieve intended properties such as fast kinetics and long-term stability. The performance of a molecular catalyst can be judged by the following figures of merit:

$$\text{Faradaic efficiency (FE)} = (\text{moles product}/\text{moles of electrons passed}) \\ \times (\text{number of electrons needed for conversion}),$$

$$\text{Overpotential} = \text{applied potential at a given current density} \\ - \text{thermodynamic potential for conversion.}$$

$$\text{Turnover number (TON)} = \text{moles intended products}/\text{moles catalyst},$$

$$\text{Catalytic selectivity (CS)} = \text{moles intended products}/(\text{moles H}_2 + \text{moles other products}),$$

$$\text{Turnover frequency (TOF)} = \text{catalytic turnovers per unit time.}$$

Further information regarding molecular catalysts for CO<sub>2</sub> reduction can be found in recently published reviews (1, 4).

## 1.4. Photochemical and Photoelectrochemical Reduction of CO<sub>2</sub>

There are several ways to reduce CO<sub>2</sub> with the assistance of renewable solar energy, and these methods can be divided into three major categories: homogeneous photoreduction by a molecular catalyst, photoelectrochemical reduction by a semiconducting photocathode, and electrochemical reduction by an electrolyzer powered by commercial photovoltaic (PV) devices.

A homogeneous CO<sub>2</sub> photoreduction system consists of a molecular catalyst, light absorber, sacrificial electron donor, and/or electron relay. When looking at these types of systems, the main figure of merit is the photochemical quantum yield, defined as

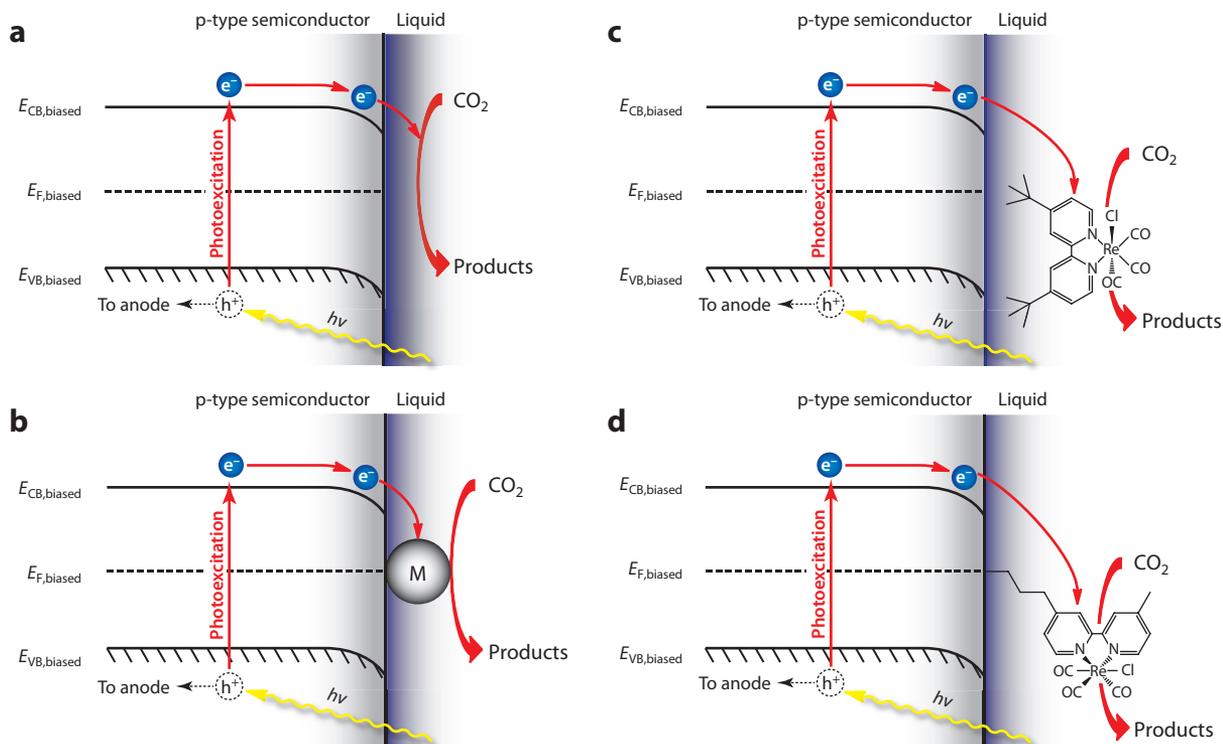
$$\text{Photochemical quantum yield } (\Phi) = (\text{moles products}/\text{absorbed photons}) \\ \times (\text{number of electrons needed for conversion}).$$

In a heterogeneous system, p-type semiconductor/liquid junctions are extensively studied as PV devices. The p-type semiconducting electrodes can act as photocathodes for photoassisted CO<sub>2</sub> reduction. **Figure 1** shows four different schemes of photoassisted reduction of CO<sub>2</sub> using a semiconducting photocathode: (a) direct heterogeneous CO<sub>2</sub> reduction by a biased semiconductor photocathode (5–26), (b) heterogeneous CO<sub>2</sub> reduction by metal particles on a biased semiconductor photocathode (6, 13, 15, 27–35), (c) homogeneous CO<sub>2</sub> reduction by a molecular catalyst through a semiconductor/molecular catalyst junction (36–43), and (d) heterogeneous CO<sub>2</sub> reduction by a molecular catalyst attached to the semiconductor photocathode surface (13, 22, 44–46).

There are several examples where PV-powered commercial electrolyzers have been used for hydrogen generation (47–49), but very few of these setups exist for CO<sub>2</sub> reduction to an energy-dense product (50–53). The idea to power an electrolyzer by a PV device was first proposed by Bard & Fox (54) for the water splitting electrolyzer. Recently, Delacourt et al. (55) reported a PV-powered electrolyzer that forms syngas (CO and H<sub>2</sub>) from CO<sub>2</sub> and water.

For these different systems, the expressions for solar to chemical energy conversion efficiency are complicated because multiple products can form at the cathode and anode. In most cases, CO<sub>2</sub> photoelectrochemical reduction on photocathodes happens at high overpotentials, which further complicates this calculation. A detailed description of the different efficiency expressions for CO<sub>2</sub> photoelectrochemical reduction is provided in **Supplemental Section 1** (follow the **Supplemental Material** link from the Annual Reviews home page at <http://www.annualreviews.org>). These

 Supplemental Material



**Figure 1**

Schematic diagrams of four different schemes for light-assisted CO<sub>2</sub> reduction on a semiconducting photocathode:

(a) heterogeneous catalysis on a semiconductor electrode, (b) heterogeneous catalysis on a metal-decorated semiconductor electrode, (c) homogeneous catalysis through a semiconductor/molecular catalyst junction, and (d) heterogeneous catalysis through a molecular catalyst-decorated semiconductor electrode.

supplemental equations can be used to calculate the efficiency for the following cell configurations: (a) a three-electrode cathodic half-cell reaction (**Supplemental Equations 1.1–1.3**), (b) a two-electrode photoelectrochemical cell (PEC) (**Supplemental Equation 1.4**), and (c) a two-electrode PV-powered electrolyzer (**Supplemental Equation 1.5**).

## 2. HOMOGENEOUS PHOTOCATALYTIC REDUCTION OF CO<sub>2</sub> WITH PHOTOSENSITIZER AND CATALYSTS

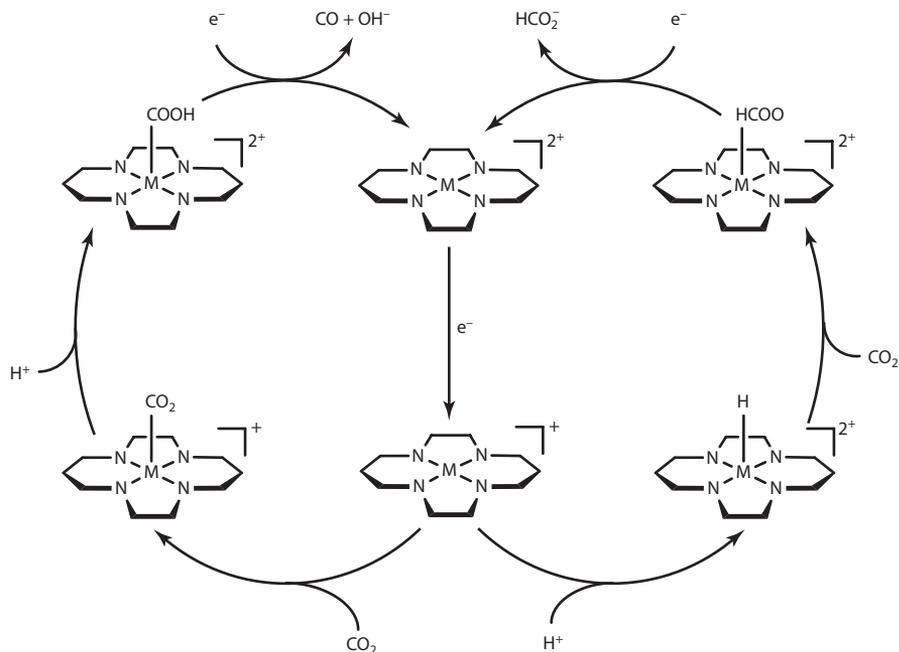
The generic mechanism of the photocatalytic reduction of CO<sub>2</sub> (Equations 6a–d, below) consists of a photosensitizer (P) capable of absorbing radiation in the ultraviolet or visible region and of the generation of an excited state (P<sup>\*</sup>). The excited state is reductively quenched by a sacrificial donor (D) generating a singly reduced photosensitizer (P<sup>-</sup>) and oxidized donor (D<sup>+</sup>). The choice of photosensitizer must be such that P<sup>-</sup> is able to transfer an electron efficiently to the catalyst species (cat) to generate the reduced catalyst species (cat<sup>-</sup>). In some cases the photosensitizer and the catalyst are the same species. The cat<sup>-</sup> is then able to bind CO<sub>2</sub> and proceed with the catalytic mechanism to release the intended products and regenerate cat. Common photosensitizers used in these systems include aromatics, e.g., p-terphenyl and phenazine, and polypyridine-coordinated transition metal complexes. Ruthenium(II) trisbipyridine ([Ru(bipy)<sub>3</sub>]<sup>2+</sup>) is the most often

employed transition metal complex due to its strong visible-light absorption and high photostability (56). The most common catalyst species include macrocycle complexes of Ni and Co, polypyridine Ru and Re catalysts, and suspended metal colloids. The macrocycle and polypyridine complexes are the most efficient and therefore the focus of this section. There have been several excellent reviews on this subject that can be referred to for further details (57–59).



Conjugated metallomacrocycles such as corrins (60), corroles (61), porphyrins (61), and phthalocyanines (62) with a Co or Fe center have been shown to act as photocatalysts for CO<sub>2</sub> reduction. Such metallomacrocycles strongly absorb visible light and do not require the addition of a photosensitizer. These systems do, however, suffer from low  $\Phi$  and low CS due to significant production of H<sub>2</sub>. Tetraazamacrocyclics such as Ni(cyclam) have proved to reduce CO<sub>2</sub> efficiently and selectively to CO electrocatalytically while adsorbed on an Hg electrode (40). In purely photocatalytic systems, however, they tend to suffer from low  $\Phi$ , CS, and TON (63, 64). When Co is used as the metal center, the photocatalytic properties are improved. In one early report, a series of cobalt tetraazamacrocycles was shown to photocatalyze the reduction of CO<sub>2</sub> using Ru(bipy)<sub>3</sub> as a photosensitizer and ascorbic acid as the sacrificial donor (65). This system displayed a reasonably high TON of 532 at very low catalyst concentrations (3.2  $\mu\text{M}$ ) but had poor selectivity (CS < 1) with H<sub>2</sub> cogeneration. Solutions of Co(III)cyclam with p-terphenyl as a photosensitizer and triethanolamine as sacrificial donors produced CO and formate as the major products, with quantum yields of 0.15 and 0.10, respectively (66). The reduction potential of the p-terphenyl radical anion is high enough to access the Co(I) state. Co(I) can then either bind CO<sub>2</sub> to form a Co-CO<sub>2</sub> adduct, which can then be protonated and reduced to produce CO and OH<sup>-</sup>, or it can react with a proton to generate a hydride to which CO<sub>2</sub> can insert to form a Co-OOCH intermediate that will then release formate upon a second reduction (**Figure 2**). The identity of the amine sacrificial donor was shown to have an effect on the product distribution because it may also act as a ligand during the catalytic cycle. Formate was produced with much higher selectivity when phenazine was used as the photosensitizer because it was shown to function as an electron and hydrogen transfer agent (67).

A well-studied catalyst, Re(bipy)(CO)<sub>3</sub>X (where bipy = 2,2'-bipyridine and X = Cl, Br), capable of selective production of CO without the use of a separate photosensitizer was developed by Lehn and coworkers (68, 69). <sup>13</sup>CO was detected when using labeled <sup>13</sup>CO<sub>2</sub>, confirming that the CO originated from the photochemical reduction of CO<sub>2</sub>. Under these conditions, however, complete exchange to the fully labeled complex Re(bipy)(<sup>13</sup>CO)<sub>3</sub>Cl was also observed. The proposed catalytic cycle (**Figure 3**) demands an empty coordination site for CO<sub>2</sub> binding. Indeed, under illumination and in the presence of an electron donor, anion exchange of Cl<sup>-</sup> with Br<sup>-</sup> occurred, indicating that loss of halide could be generating the open coordination site. Adding excess X<sup>-</sup> ligand was shown to increase efficiency and stabilize CO production by inhibiting a competing mechanism in which halide loss, formation of a Re hydride, and CO<sub>2</sub> insertion leads to the formate complex, Re(bipy)CO<sub>3</sub>(HCOO) (69). With the addition of phosphate groups to the Re(bipy)(CO)<sub>3</sub>X system (X = P(OEt)<sub>3</sub>), one of the highest single-molecule quantum efficiencies was reported for a homogeneous photocatalytic system ( $\Phi = 0.38$ ) (70). In a two-molecule system consisting of a 25:1 mixture of Re(bipy)(CO)<sub>3</sub>(P(OMe)<sub>3</sub>) as photosensitizer and Re(bipy)(CO)<sub>3</sub>MeCN as catalyst, even higher quantum yields were achieved ( $\Phi = 0.59$ ) (71). Triethanolamine was used



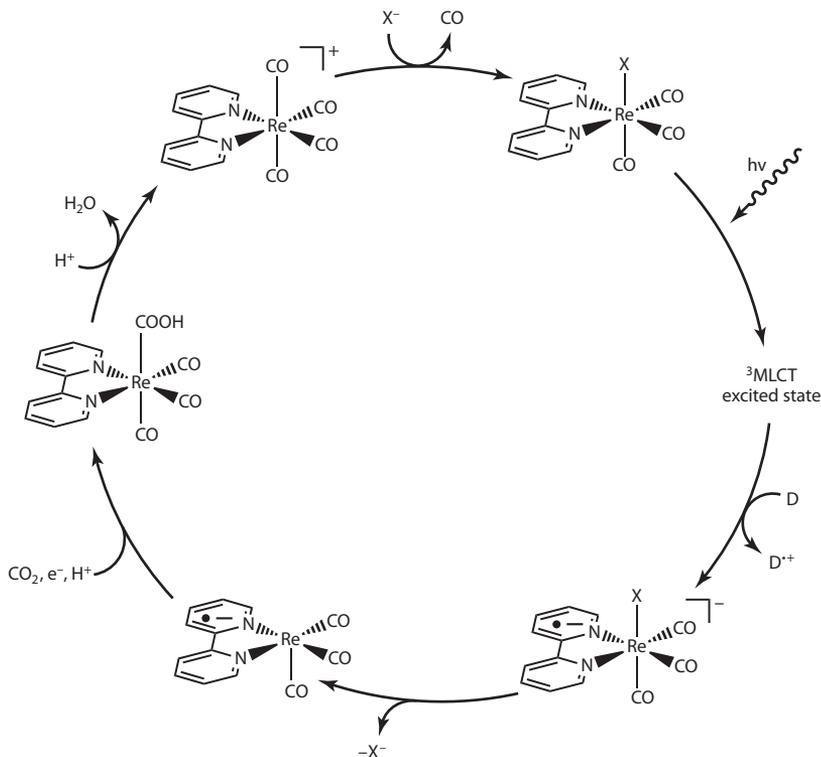
**Figure 2**

Proposed mechanism for CO and formate production from photocatalyzed reduction of CO<sub>2</sub> by tetraazamacrocycle transition metal complexes (M = Co, Ni).

as a sacrificial donor. The MeCN ligand on the [Re(bipy)(CO)<sub>3</sub>MeCN]<sup>+</sup> complex is labile and easily generates an open CO<sub>2</sub> binding site. The [Re(bipy)(CO)<sub>3</sub>(P(OMe)<sub>3</sub>)]<sup>+</sup> was chosen as the photosensitizer due to its efficient conversion to the reduced species.

Although the Re catalyst systems mentioned above demonstrated remarkable  $\Phi$ , they lacked extended absorption in the visible region. For practical purposes, such as utilization of solar photons, absorption in the visible is desired. Ishitani and coworkers (72) have addressed this issue by utilizing a bridging ligand to covalently attach a [Ru(bipy)<sub>3</sub>]<sup>2+</sup>-type photosensitizer, which absorbs strongly in the visible, to a Re(bipy)(CO)<sub>3</sub>X type catalyst to create a supramolecular dyad complex. This dyad exhibited significantly better performances ( $\Phi = 0.12$ , TON = 170) relative to a simple, noncovalently linked mixture of the photosensitizer and catalyst ( $\Phi = 0.062$ , TON = 101), which the authors ascribe to more efficient intramolecular electron transfer from the reductively quenched Ru(bipy)<sub>3</sub>-type species to the Re(bipy)(CO)<sub>3</sub>X as compared with the intermolecular electron transfer that occurs for the mixture system. A subsequent publication reported the effect of the bridging ligand on the performance of the supramolecular catalyst: A  $\Phi$  of 0.21 was achieved, which was the best reported value in homogeneous photocatalytic systems using low energy visible light > 500 nm (73).

Although the systems described above primarily produced CO as a CO<sub>2</sub> reduction product, it is worth noting that several systems selectively produce formate using Ru(bipy)<sub>2</sub>XY (X = Y = CO) (74) (X = CO, Y = H) (75) in conjunction with Ru(bipy)<sub>3</sub> as the photosensitizer. The product formation was shown to be dependent on the presence of water and the identity of the sacrificial electron donor (74). A recent publication has examined the pathway for formate production using density functional theory (DFT) on a Re(bipy)(CO)<sub>3</sub>Cl catalyst with triethylamine (TEA) as the



**Figure 3**

Proposed photocatalytic mechanism for CO production from a  $\text{Re}(\text{bipy})(\text{CO})_3\text{X}$  catalyst. Abbreviation: MLCT, metal-to-ligand charge transfer.

sacrificial donor (76). The net catalytic cycle for formate production was predicted to be exothermic by 36.4 kcal/mol.

Although photocatalytic reduction of  $\text{CO}_2$  may become an important stepping stone to solar fuel production, much progress remains before it becomes practical as an industrial process. Presently, TONs remain in the hundreds and TOFs are typically in the tens per hour. More mechanistic work must be done in order to understand and increase the stability and rates of these systems. These quantitative measures of catalytic systems must also be scrutinized because they are dependent on catalyst concentration and can vary drastically depending on the concentrations and volumes chosen for the experiment. TON can be especially misinterpreted because it is often not reported whether the catalytic activity stopped at the given TON or if the experiment was simply ended after a given time. To compound the problem, different solvents, electron donors, photosensitizers, and light sources are employed by the various groups studying these photocatalysts. A more uniform system of measure may be needed in order to fairly compare these catalyst systems.

Looking forward to improved systems with a more practical utility, we must consider some additional issues. Since many of the photocatalysts presently studied are metal complexes employing rare and expensive transition metals, it is especially important to raise the catalytic rate and long-term stability to make this process economically feasible. More work must be done using earth-abundant elements that could support large-scale undertakings such as solar fuel production.

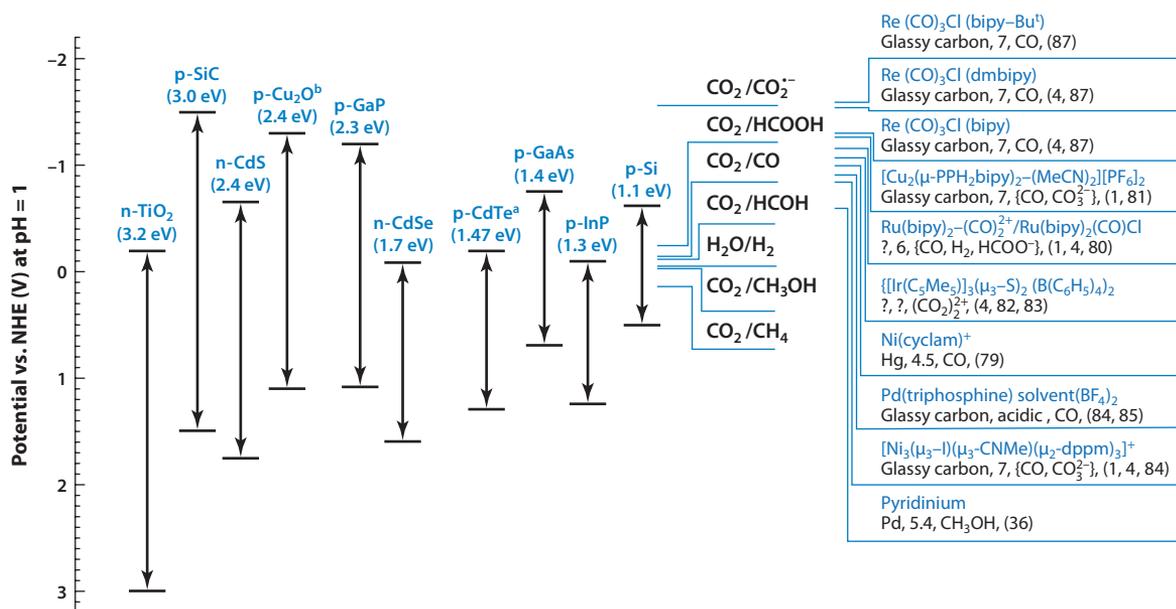
Another drawback to the reviewed systems is the use of a sacrificial donor to supply the electrons for the reduction process. Ideally, water would be the source of both the electrons and hydrogen atoms for CO<sub>2</sub> reduction catalysis in an artificial photosynthetic process. These issues are not trivial and will take considerable effort and creativity to solve.

### 3. HETEROGENEOUS PHOTOELECTROCHEMICAL REDUCTION OF CO<sub>2</sub> ON SEMICONDUCTOR PHOTOCATHODES

Heterogeneous photoelectrochemical reduction of CO<sub>2</sub> on semiconductor surfaces has been explored extensively in the last three decades. **Figure 4** shows band edge positions versus an NHE for several common p- and n-type semiconductor electrodes with CO<sub>2</sub> reduction potentials for different products at pH = 1. The single-electron reduction of CO<sub>2</sub> to CO<sub>2</sub><sup>-</sup> is above the conduction band of most of the semiconductors shown in the figure. Thermodynamically, proton-assisted multielectron reduction potentials for CO<sub>2</sub> lie within the band gap of several semiconductors. However, kinetic limitations lead to high overpotential for electrochemical reduction of CO<sub>2</sub> on semiconductor photocathodes or dark cathodes, as tabulated in **Supplemental Table 1**.

▶ Supplemental Material

Both aqueous (5, 6, 8, 11, 14–16, 22, 25–28, 34, 42, 91, 92) and nonaqueous (7, 10, 12, 13, 17–20, 23, 24, 29, 31–33) solvents have been used for direct CO<sub>2</sub> photoelectrochemical reduction on flat semiconductor surfaces, with the most commonly reported nonaqueous solvents being polypropylene carbonate, acetonitrile, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and



**Figure 4**

Position of the conduction and valence bands of several semiconductors at pH = 1 versus a normal hydrogen electrode (NHE) (77, 78). Thermodynamic potentials for CO<sub>2</sub> reduction to different products at pH = 1 versus an NHE are shown beside the band edge positions of semiconductors. CO<sub>2</sub> reduction potentials of the homogeneous catalysts are shown at the right. Information presented here (in the form of catalyst, electrode used, pH, product, references) and detailed information about the homogeneous catalysts can be found in References 1, 4, 36, and 79–87. Band edges for p-CdTe are given in Reference 88. Band edges for p-Cu<sub>2</sub>O are given in References 89 and 90.

methanol. The greatest difference between water and nonaqueous solvents is the solubility of CO<sub>2</sub>. In nonaqueous solvents, the solubility is 7–8 times higher than in water (10, 93, 94). Methanol, for example, is known to be a physical absorber of CO<sub>2</sub> and is presently used in the Rectisol process in industrial plants (20, 31, 32). Aqueous media further complicate CO<sub>2</sub> reduction, as different CO<sub>2</sub> hydration products are present in water. In water, CO<sub>2</sub> hydration occurs to form carbonic acid, which then undergoes stepwise dissociation to bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>). The predominant species is pH-dependent: CO<sub>2</sub> is dominant at pH < 4.5; HCO<sub>3</sub><sup>-</sup> is dominant at 7.5 < pH < 8.5; and CO<sub>3</sub><sup>2-</sup> is dominant at pH > 11.5 (95). This, in turn, affects the thermodynamic potentials for generating certain products, as they are dependent on the form of CO<sub>2</sub> present in solution.

Water, however, is commonly used as a proton source in aprotic solvents for CO<sub>2</sub> reduction. In one study (96), CO<sub>2</sub> solubility was shown not to change with the addition of up to 1% (500 mM) water to acetonitrile but drastically decreased with higher water concentrations. DMF and DMSO performed better than polypropylene carbonate and acetonitrile when mixed with 1% water, as they were better able to suppress competing proton reduction processes (10). Many other differences between aqueous and nonaqueous solutions are factors in efficient CO<sub>2</sub> reduction apart from those mentioned and are discussed further in Section 3.3.

The limitations of CO<sub>2</sub> solubility in water at standard pressures as well as its diffusion limitations set a maximum catalytic current density of 10 mA cm<sup>-2</sup> for electrochemical reduction of CO<sub>2</sub> (27, 94). CO<sub>2</sub> solubility, and thus maximum catalytic current, can be increased using high-pressure CO<sub>2</sub> environments. High-pressure CO<sub>2</sub> environments offer high catalytic current density and high selectivity over proton reduction for both metal (97, 98) and semiconductor (25, 26) electrodes. Gas-diffusion electrodes (99, 100), as well as other options, have also been explored to increase CO<sub>2</sub> concentration, which is imperative to increase catalytic current densities.

Several metal electrodes have been used for catalytic reduction of CO<sub>2</sub> in both aqueous and nonaqueous media. The catalytic activity of a metal catalyst can be transferred to semiconductor photocathodes through discontinuous films of metals without sacrificing photovoltage. The objective of this approach is to incorporate the stability and catalytic activity of metal particles with semiconducting photocathodes. In a truly photoelectrocatalytic system, when a photoelectrode coupled to a catalyst (metal particles) is run under illumination, the FE versus applied potential has similar behavior to the catalyst alone with a positive shift in the onset voltage called the photovoltage shift. Apart from the photovoltage shift, catalytic activity and product distribution should not be affected by illumination. A detailed description of this type of system is provided in **Supplemental Section 2**.

Surface plasmon effects of nanometallic particles on semiconductor surfaces have not been considered for this type of photocatalytic system, and an introductory note on this topic is included in **Supplemental Section 3**.

### 3.1. Aqueous Media

Studies by Junfu & Baozhu (15) of CO<sub>2</sub> reduction at (111) p<sup>+</sup>/p-Si to formate agree with the selectivity at inert electrodes proposed by Amatore & Savéant (104). In this study by Junfu & Baozhu, the incident illumination intensity was varied up to as high as 73 mW cm<sup>-2</sup>, though no dark measurements were taken and no flat band potential was reported. The reduction was done in 0.5 M NaSO<sub>4</sub> under a bromine tungsten lamp. At lower pH, proton reduction to hydrogen dominated (FE for CO<sub>2</sub> < 5%, pH ~ 6), whereas at high pH, CO<sub>2</sub> solubility diminished. Neutral pH yielded ideal conditions for reducing CO<sub>2</sub> with p-Si. The maximum FE was reported to occur at -1.2 V versus a saturated calomel electrode (SCE), but actual values were not given. HCOOH

(FE = 21%) was produced at  $-1.6$  V versus SCE. Electroplated Pb particles prevented proton reduction and shifted the onset of  $\text{CO}_2$  reduction positively by 100 mV.

Both p- and n-type GaAs have been used for direct photoelectrochemical reduction of  $\text{CO}_2$  and are well known for their ability to produce methanol (101). The mechanism for methanol production has been contentious for years. Sears & Morrison demonstrated that regardless of illumination or applied bias,  $(-1 -1 -1)$  arsenic-rich surfaces of GaAs spontaneously produce  $\text{CH}_3\text{OH}$ , even under conditions of no net current (101). They attributed this to the corrosion of the electrode, which had no effect on the faradaic product,  $\text{HCOOH}$  (FE  $\sim 100\%$ ) at  $-0.8$  V versus Ag/AgCl.

Reduction of  $\text{CO}_2$  on illuminated (111) surface p-CdTe and (100) surface p-InP was performed with various electrolytes at  $-1.2$  V versus SCE (11). InP was found to be more selective for proton reduction (FE  $\geq 60\%$ ) than was CdTe (FE  $\geq 38\%$ ). When tetraalkylammonium electrolytes were used, proton reduction to  $\text{H}_2$  decreased on both CdTe (FE  $\geq 10\%$ ) and InP (FE  $\geq 25\%$ ). Yoneyama et al. (11) attributed this to tetraalkylammonium inhibiting proton adsorption by making the electrodes more hydrophobic. Running at more negative potentials decreased selectivity for CO and raised selectivity for both  $\text{HCOOH}$  and  $\text{H}_2$ .  $\text{CO}_2$  reduction performed at  $0^\circ\text{C}$  increased  $\text{CO}_2$  solubility, which increased CO and  $\text{HCOOH}$  production. When carbonate electrolytes were used,  $\text{HCOOH}$  selectivity increased, whereas CO selectivity greatly decreased. This can be understood by considering the reaction of  $\text{CO}_2^-$  to CO: two disproportionate  $\text{CO}_2^-$  radical anions forming CO and  $\text{CO}_3^{2-}$ . In the presence of an excess of  $\text{CO}_3^{2-}$ , the back reaction suppresses CO production.

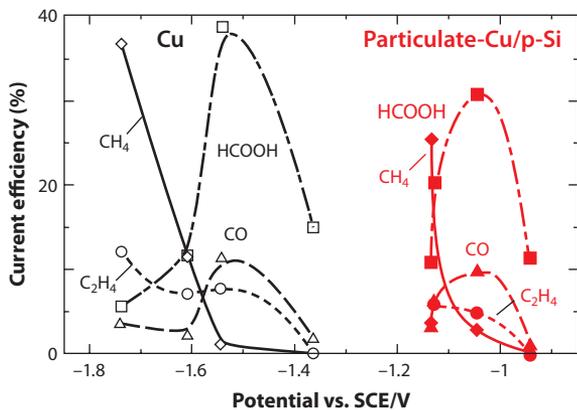
High-pressure reduction of  $\text{CO}_2$  on illuminated p-GaAs and (111) plane p-GaP was performed at various potentials and electrolyte conditions (25). On (111) plane p-GaAs at 1 atm of  $\text{CO}_2$  and 0.5 M KCl,  $\text{CO}_2$  was reduced at  $-1.29$  V versus SCE to  $\text{HCOOH}$  (FE = 6.7%) and  $\text{HCHO}$  (FE = 0.59%). At  $-1.84$  V versus SCE, only  $\text{HCOOH}$  (FE = 15.2%) was produced. On (111) p-GaP at 3 atm  $\text{CO}_2$ , with  $\text{HClO}_4$  as the supporting electrolyte, total  $\text{CO}_2$  reduction gave a low FE (18%) at  $-1.00$  V versus Ag/AgCl but produced a large amount of  $\text{CH}_3\text{OH}$  (FE = 7.2%). With  $\text{Na}_2\text{CO}_3$  as the supporting electrolyte, reduction of  $\text{CO}_2$  at 3.5 atm peaked, with a total FE of 80% at  $-1.00$  V versus Ag/AgCl and with  $\text{HCOOH}$  as the main product (FE = 74%). Repeating this experiment at 7.5 atm dropped  $\text{HCOOH}$  selectivity dramatically (FE = 29%), but methanol selectivity increased (FE = 8.2%). The shift toward proton reduction may be attributed to the increased concentration of carbonic acid.

$\text{TiO}_2$  has also been used as a photoelectrode at high pressures with marginal results (26). The highest FE achieved for  $\text{CO}_2$  reduction occurred at 8 atm  $\text{CO}_2$  at  $-1.84$  V versus Ag/AgCl with  $\text{HCOOH}$  as the main product (FE = 22%).

Hinogami and coworkers (27, 91, 92) reported photoelectrochemical reduction of  $\text{CO}_2$  on Cu, Ag, and Au nanoparticles attached to (100) p-Si. On particulate-Cu/p-Si electrodes, the expected voltage-dependent FEs and discrete photovoltage shifts were obtained under illumination. Cu is a unique catalyst, as it can readily reduce  $\text{CO}_2$  beyond  $\text{HCOOH}$  and CO at higher applied potentials (102). **Figure 5** shows the FE of different products on illuminated particulate-Cu/p-Si photocathodes and dark Cu cathodes versus applied potential. It is evident from the figure that photogenerated electrons are available to particulate-Cu/p-Si for  $\text{CO}_2$  reduction with a photovoltage shift of 500 mV versus bare Cu. Similar behavior was observed with particulate-Ag/p-Si and particulate-Au/p-Si photocathodes (tabulated in **Supplemental Table 1**) (27).

Electrodes utilizing Cu and Ru particles on p-GaP have been used to reduce  $\text{CO}_2$  under illumination (28). Flaisher et al. (28) employed chopped illumination with both sub-band gap excitations and higher than band gap excitations. At an applied potential of  $-1.54$  V versus SCE, trace amounts of  $\text{HCOOH}$  were seen, but mostly  $\text{H}_2$  was produced. Current enhancement was seen for  $\text{CO}_2$  reduction with both Cu and Ru.

 Supplemental Material



**Figure 5**

Current efficiencies versus potential for various CO<sub>2</sub> reduction products after potentiostatic electrolyses on particulate-Cu/p-Si and Cu-metal electrodes. Note the similarity in reduction behavior offset by approximately 500 mV. Reprinted with permission from Reference 27. Copyright 1998 American Chemical Society. Abbreviation: SCE/V, saturated calomel electrode per volt.

Some semiconductor materials are not suited for direct contact with aqueous solution due to spontaneous corrosion, but there is still much room for further investigation with semiconductor electrodes, both bare and in conjunction with catalysts.

### 3.2. Nonaqueous Media

The reduction potentials, current densities, product distributions, and FEs of CO<sub>2</sub> photoelectrochemical reduction on p-Si (10, 17, 33), p-InP (10, 17, 20, 30), p-GaAs (10, 17, 20), and p-GaP (10) in various nonaqueous solvents are tabulated in **Supplemental Table 1**. The main product for CO<sub>2</sub> reduction in most nonaqueous solvents on these semiconductor surfaces was CO with varying FE, except in methanol with a p-GaAs photocathode. In the latter configuration, HCOOH and CH<sub>3</sub>COOH were produced with FE similar to that of CO (17). These products are consistent with the CO<sub>2</sub> reduction mechanism proposed for metal electrodes in nonaqueous media in the literature (103). In these cases, comparison between the onset potential of CO<sub>2</sub> reduction and catalytic current density on various semiconductor surfaces is not feasible due to lack of information about illumination intensity.

Much work has been done on p-CdTe photocathodes for CO<sub>2</sub> photoelectrochemical reduction in nonaqueous media by Bockris and coworkers (7, 10, 12, 13, 23, 24). Photoelectrochemical reduction of CO<sub>2</sub> to CO was achieved on (100) p-CdTe at a potential 600–700 mV less negative than a In cathode with 80–85% FE and unit quantum efficiency using 600-nm monochromatic illumination in DMF–5% water with 0.1 M of tetrabutylammonium phosphate (12, 24). When compared with other p-type semiconductors like p-Si, p-GaP, p-InP, and p-GaAs, CdTe was notable for its low CO<sub>2</sub>–reduction-onset potential and high quantum efficiency (10). Catalytic current increased with both light intensity (600 nm wavelength, 32 mW cm<sup>-2</sup>) and CO<sub>2</sub> partial pressure up to 0.5 atm on p-CdTe (10). Saturation of catalytic current and maximum photovoltage occurred at approximately 0.5 atm, which may have been limited by the incident light intensity (32 mW cm<sup>-2</sup>). A FE of 80–85% was observed for DMF, DMSO, and PC with 5% water as the solvent, whereas acetonitrile had a FE approximately 60% due to its protophobic nature that favors proton reduction (10).

Higher-pressure CO<sub>2</sub> (40 atm) was employed for nonaqueous systems to further improve the catalytic current density. Most efforts using this approach utilized methanol as the solvent (17–19). Only three types of semiconductors (p-Si, p-GaAs, p-InP), each using the (100) surface, were investigated, with the primary focus on (100) p-InP. For (100) p-InP, a catalytic current density of 100–200 mA cm<sup>-2</sup> was achieved. Photoelectrochemical reduction of CO<sub>2</sub> was limited by light intensity and not mass transport of CO<sub>2</sub> (17). Apart from enhanced catalytic current density, the high CO<sub>2</sub> pressure also provided better selectivity for CO<sub>2</sub> over proton reduction for all three semiconducting photocathodes, with the main product being CO. For p-InP, the photostability improved significantly under high CO<sub>2</sub> pressure.

Similar to aqueous media, p-type semiconductors decorated with metal nanoparticles were also examined in nonaqueous solvents for CO<sub>2</sub> photoelectrochemical reduction. Various metal nanoparticles were explored on p-type semiconductors such as p-Si (33), p-InP (30–32), p-GaP (29), and p-CdTe (13). For particulate-Cu/p-Si in 3 M H<sub>2</sub>O in acetonitrile, products such as CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> were observed with a photovoltage shift of 500 mV with respect to Cu (33). These products are characteristic of CO<sub>2</sub> reduction on Cu electrodes. The major product of CO<sub>2</sub> reduction in methanol on a p-InP photocathode modified with metal particles of Au, Ag, Pd, Cu, and Ni was CO, whereas for particulate-Pb/p-InP, the major product was HCOOH (31). A product yield comparison between particulate-Cu/p-InP and particulate-Pb/p-InP suggested that Cu was not acting catalytically on the semiconducting electrode, whereas Pb was. Much improvement is needed in this type of system for CO<sub>2</sub> photoelectrochemical reduction. Most critically, integration of a metal particle's catalytic activity on a p-type semiconductor electrode must be improved to minimize loss of photovoltage.

### 3.3. The Mechanism of CO<sub>2</sub> Reduction on Semiconductor Surfaces

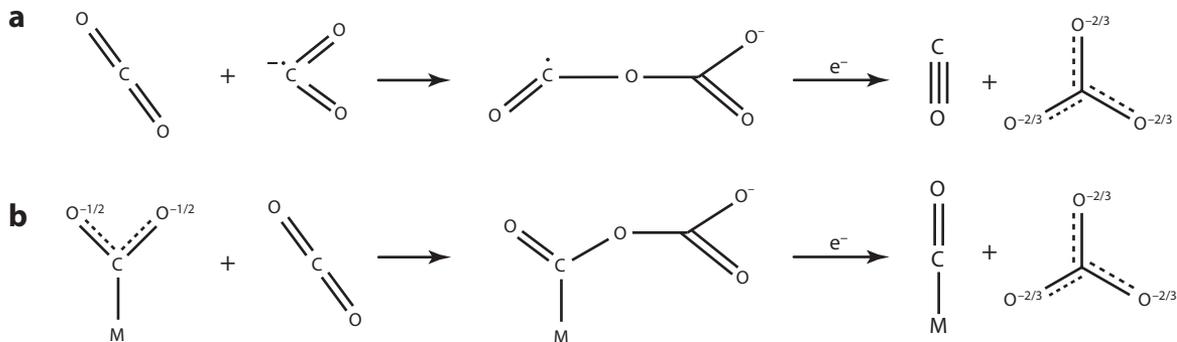
The three primary products of the reduction of CO<sub>2</sub> are oxalate [(CO<sub>2</sub>)<sub>2</sub><sup>2-</sup>], CO, and HCOO<sup>-</sup>/HCOOH. In aqueous solutions and on electrodes not selective for oxalate or CO, HCOO<sup>-</sup> is the main product. In nonaqueous solutions with relatively low proton concentrations, CO and oxalate are the primary products.

Amatore & Savéant (104) offered some of the earliest mechanistic discussions on selectivity in aqueous media. They stated that on inert electrodes HCOO<sup>-</sup>/HCOOH is the main product. On some electrodes like Cu, CO<sub>2</sub> can be reduced as far as ethanol and methane and the selectivity for these products can be directed by adjusting the working electrode potential (27, 103).

The most energetically demanding and often rate-limiting step is the initial reduction of CO<sub>2</sub> to CO<sub>2</sub><sup>-</sup>. Adsorption onto an electrode surface can allow for both heterogeneous electron transfer and stabilization of the CO<sub>2</sub><sup>-</sup> species. On transition metals, stabilization occurs through back-bonding from d-orbitals to the antibonding π\* orbital of CO<sub>2</sub> (103). This back-donation tends to favor side-on or C-coordinated adsorption.

There is disagreement about whether the many steps involved in CO<sub>2</sub> reduction occur through adsorbed species or in solution away from the surface. Although much work has already been done to discover the intermediates and products involved, the large number of proposed mechanisms shows that more definitive studies are required. For example, Hori et al. (103) and Jitaru et al. (106) disagree on the mechanism for formate production on sp group metals. Although both agree that water is deprotonated by CO<sub>2</sub><sup>-</sup> to form the carboxyl radical formyloxyl (HCO<sub>2</sub>·), they disagree about whether or not this radical remains adsorbed onto the electrode surface. CO<sub>3</sub><sup>2-</sup> and OH<sup>-</sup> concentrations with respect to HCOO<sup>-</sup> production are not discussed in these studies.

Amatore & Savéant (104) also discuss the competing pathways for the primary CO<sub>2</sub> reduction products in media of low proton availability. Their kinetic studies on Pb and Hg electrodes show



**Figure 6**

(a) The Savéant-proposed mechanism and (b) the Hori-proposed mechanism for CO production in low proton concentrations or high CO<sub>2</sub> concentrations (103).

that oxalate production occurs through spontaneous formation of a carbon-carbon bond between CO<sub>2</sub><sup>-</sup> anions in solution. For CO, they propose a dimer wherein CO<sub>2</sub><sup>-</sup> bonds with unreduced CO<sub>2</sub> to form an oxygen-carbon bond as depicted in **Figure 6a**. Upon a second reduction, disproportionation of the dimer to CO and CO<sub>3</sub><sup>2-</sup> occurs. For HCOO<sup>-</sup>, the authors propose that CO<sub>2</sub><sup>-</sup> and water react to form HCO<sub>2</sub><sup>-</sup> and OH<sup>-</sup>. Upon a second reduction of the HCO<sub>2</sub><sup>-</sup> radical, HCOO<sup>-</sup> is produced.

Hori et al. (103) propose that C-coordinated CO<sub>2</sub> on metal electrodes may have similar properties to CO<sub>2</sub> in the Ni(cyclam)Cl<sub>2</sub> catalyst system. They state that electron density is pushed onto the O atoms as opposed to the C atom. As such, the O atoms can form bonds with hydrogen atoms or C atoms from CO<sub>2</sub>.

Tryk et al. (105) used calculations and Tafel plots for CO<sub>2</sub> reduction on InP and particulate metal/carbon electrodes to support the hypothesized intermediate shown in **Figure 6a**. Their thermodynamic calculations for the gaseous species of CO<sub>2</sub><sup>-</sup> and the radical dimer yield a stabilizing energy equivalent to a positive voltage shift of 1.5 V upon dimerization. The authors also demonstrate that tetrabutylammonium ions can increase selectivity for CO<sub>2</sub> reduction on electrode surfaces by making the surface more hydrophobic. Additionally, they propose that surfaces capable of adsorbing CO<sub>2</sub> into a matrix of T-coordinated molecules assist in photoelectrochemical reduction of CO<sub>2</sub> to CO.

Jitaru et al. (106) and Hara et al. (99) both correlate catalytic selectivity to elemental groups of metals. Extensive work on semiconductor electrode materials has not been done, but these studies on metals may shed light on how reduction occurs on plain semiconductor electrodes. The orbital character of the studied electrodes is a good predictor of selectivity. In aqueous solutions, sp metals and d<sup>10</sup> metals are selective for HCOO<sup>-</sup>, whereas d metals are more selective toward CO (97, 106). In nonaqueous media, some sp metals are selective for oxalate, whereas some sp and most d metals are selective for CO (106).

Cu in particular is a unique metal as it can efficiently reduce CO<sub>2</sub> past CO, as adsorbed CO does not easily poison its surface. To understand this mechanism, Peterson et al. (107) used density functional theory to evaluate the free energy landscape for reduction and protonation of adsorbed CO. Their model, which accounts for adsorption sites of protons and the adsorbed products, is in agreement with faradaic selectivity demonstrated in other literature. For a thorough discussion of CO<sub>2</sub> reduction on Cu, refer to Gattrell et al. (102).

## 4. PHOTOELECTROCHEMICAL REDUCTION OF CO<sub>2</sub> BY SEMICONDUCTOR/MOLECULAR CATALYST JUNCTIONS

The thermodynamic potentials for the proton-assisted multielectron reduction of CO<sub>2</sub> lie within the band gap of the semiconductors (Figure 4). However, managing these multielectron multi-proton processes requires a molecular electrocatalyst. Most molecular electrocatalysts for CO<sub>2</sub> reduction operate at a fixed pH, typically under acidic conditions. For several semiconductors, the flat band potential is also a function of pH. The variation is typically 0.059 V/pH units in accordance with the Nernst equation and reflects a change in the voltage across the Helmholtz layer, which is particularly true for semiconductors like InP, GaAs, GaP, and TiO<sub>2</sub> (77, 108). Despite this projected variation, the reduction potential of most molecular electrocatalysts might still be above the conduction band of p-type semiconductors as shown in Figure 4.

For ideal semiconductor/liquid junctions, no photoreduction of the redox species above the conduction and below the valence band edge should exist. It has been shown before, however, that the photoreduction of species with redox potentials more negative than the conduction band edges of p-type semiconductors (Ge, Si, InP, GaAs) is feasible (109–112). This phenomenon is explained by Fermi-level pinning and/or unpinning of the band edges, which causes the photovoltage observed for a p-type semiconductor/liquid junction to become independent of the redox potentials of the electroactive species. This pinning leads to photoreduction of molecular electrocatalysts, even if the reduction is above the conduction band edge of the p-type semiconductor, which was shown for the p-Si/Re(bipy-Bu<sup>+</sup>)(CO)<sub>3</sub>Cl molecular catalyst junction (37). It can be concluded that as long as the reduction potential of the molecular catalyst is above the valence band edge of the p-type semiconductor, the photoreduction of the molecular electrocatalyst is feasible. Fermi-level pinning also places a limitation on the maximum photovoltage/open circuit voltage for a particular semiconductor/liquid junction to one-half the band gap of the semiconductor (109–112). The stability of the semiconductor photocathode can be further enhanced by surface modification, either by covalent attachment or coating the surface with polymer films of the molecular electrocatalyst. Critical properties and characteristics of photoelectrochemical reduction of CO<sub>2</sub> using semiconductor/molecular electrocatalyst junctions reported in the literature are tabulated in Supplemental Table 2.

▶ Supplemental Material

### 4.1. Homogenous CO<sub>2</sub> Photoreduction Through p-Type Semiconductor/Molecular Junctions

Bradley & Tysak (113) first showed stable photoreduction of tetraazomacrocyclic metal complexes on a p-Si photocathode. For p-Si/molecular electrocatalyst junctions, photovoltages of 350–400 mV were observed with light to electrical energy conversion efficiency of 0.5 to 1% under noncatalytic conditions. These reduced tetraazomacrocyclic metal complexes were later shown to catalyze the photoreduction of CO<sub>2</sub> to CO on illuminated p-Si (43). The highest efficiency achieved in this system (2 CO:1 H<sub>2</sub>, FE = 95 ± 5%) was obtained with 18 mM of [(Me<sub>6</sub>[14]aneN<sub>4</sub>)Ni<sup>II</sup>]<sup>2+</sup> as a molecular catalyst in 1:1 acetonitrile–water solution with 0.1 M LiClO<sub>4</sub> as the supporting electrolyte. However, in completely dry acetonitrile with 0.1 M tetrabutyl ammonium perchlorate, only an equimolar amount of CO and CO<sub>3</sub><sup>2-</sup> was observed at –1.3 V versus SCE. No information regarding illumination intensity or catalytic current density was provided, making it difficult to calculate efficiency.

Zafrir et al. (42) studied the vanadium V(II)/V(III) redox couple in a highly acidic aqueous medium (114, 115) for photoreduction of CO<sub>2</sub> on a p-GaAs photocathode. V(II) does not electrocatalytically reduce CO<sub>2</sub>, which resulted in poor FEs of less than 2% (42). Parkinson & Weaver

(41) overcame this by introducing a formate dehydrogenase enzyme as a catalyst for CO<sub>2</sub> reduction to formate. In this work, the enzyme was used in conjunction with methyl viologen (MV) as an electron relay on a p-InP photoelectrode (41). The advantages of a p-InP/(MV<sup>2+</sup>/MV<sup>1+</sup>)/biological catalyst system are low overpotential for CO<sub>2</sub> reduction, selectivity, and excellent FE. The disadvantages of this system include instability of the formate hydrogenase enzyme and low efficiency.

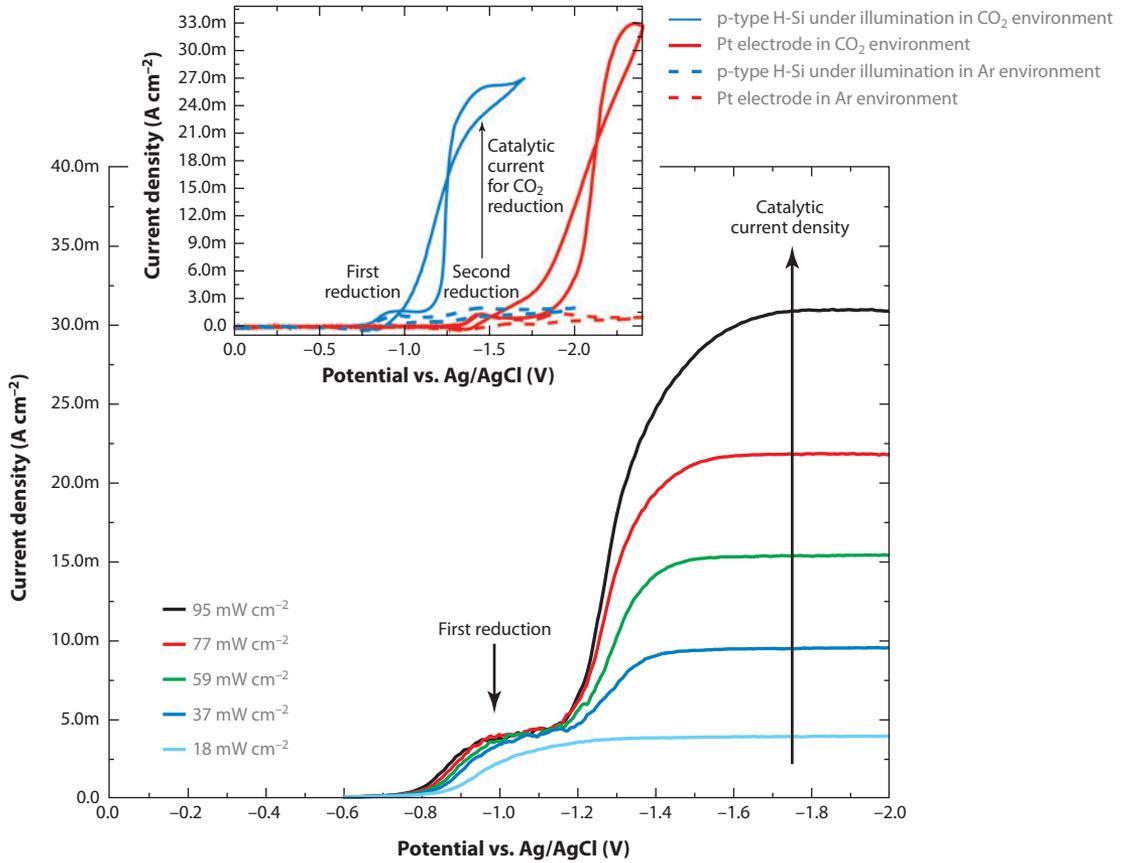
Tinnemans et al. (65) reported CO<sub>2</sub> photoreduction by p-GaP/ and p-GaAs/tetraaza-macrocyclic Co(II) and Ni(II) junctions. However, no stable photoreduction of the catalysts was observed on p-GaP and no photovoltage was observed for the p-GaAs/catalyst junction. Beley et al. (40) and Petit et al. (39) also reported the photoreduction of CO<sub>2</sub> on p-GaAs and p-GaP photocathodes with Ni(cyclam)<sup>2+</sup> (cyclam = 1,4,8,11-tetraazacyclotetradecane) as the molecular catalyst. A comprehensive review and further investigation was reported later by Petit et al. (38) on p-GaAs (111) and p-GaP (111)/Ni(cyclam)<sup>2+</sup> molecular catalyst junctions in aqueous media. CO<sub>2</sub> photoreduction with Ni(cyclam)<sup>2+</sup> on p-GaP was achieved as low as 200 mV below the thermodynamic potential for CO<sub>2</sub> to CO reduction, at -0.2 V versus an NHE. Selectivity of CO over H<sub>2</sub> was found to be between 1 and 2 for p-GaAs and between 5 and 10 for p-GaP with a FE of 80–100% (38–40). The difference in selectivity for p-GaAs and p-GaP could be due to their inherent surface chemistry characteristics. The best performance was observed for 5 mM of catalyst at 20 mW cm<sup>-2</sup> light intensity, which was explained by the occupation of accessible sites on the semiconductor surface by Ni(cyclam)<sup>2+</sup> or other intermediate species. No efficiency data were provided for this case. More work is necessary to fully understand the potential of the p-type semiconductor/Ni(cyclam)<sup>2+</sup> system.

Barton et al. (36) reported another system consisting of a p-GaP (111) photocathode and a soluble pyridinium molecular catalyst for direct selective photoreduction of CO<sub>2</sub> to methanol at 300 mV of underpotential at pH 5.2 with 63–100% FE. In this system, an overall conversion efficiency of 11% was achieved using an illumination wavelength of 365 nm at 6.5 mW cm<sup>-2</sup>. FE of methanol formation decreased and catalytic current density increased as the applied underpotential decreased, which was explained by competing proton/water reduction processes. Apart from p-GaP, pyridinium was only active with platinum group metal electrodes and inherently has low catalytic current density and FE for methanol formation.

Selective photoreduction of CO<sub>2</sub> to CO using a hydrogen terminated p-Si/Re(bipy-Bu<sup>t</sup>)(CO)<sub>3</sub>Cl (bipy-Bu<sup>t</sup> = 4,4'-di-tert-butyl-2,2'-bipyridine) molecular catalyst junction was recently reported with a photovoltage exceeding 600 mV (37). The system had a FE of 97 ± 3% for selective photoreduction of CO<sub>2</sub> to CO. Around 10% of the light energy was used for the photoreduction using either polychromatic or monochromatic light (661 nm) with a maximum catalytic current density of 31 mA cm<sup>-2</sup>. The most important aspect of this system was that the catalytic current density was only limited by the monochromatic light intensity (661 nm) up to 95 mW cm<sup>-2</sup> (Figure 7).

## 4.2. Theoretical Treatment of Homogenous CO<sub>2</sub> Photoreduction Through p-Type Semiconductor/Molecular Junctions

Figure 8 shows a schematic of photoelectrochemical CO<sub>2</sub> reduction by a p-type semiconductor/molecular junction using p-Si and Re(bipy-Bu<sup>t</sup>)(CO)<sub>3</sub>Cl as an example. There are three critical steps involved in this process: (a) charge carrier generation and separation in the semiconductor, (b) heterogeneous charge transfer to the molecular electrocatalyst, and (c) homogeneous catalysis. The total photocurrent density at an illuminated p-semiconductor/liquid junction (assuming no recombination of photogenerated carriers within the diffusion layer and fast charge transfer



**Figure 7**

Current density-voltage characteristic of a hydrogen-terminated p-Si/Re(bipy-Bu<sup>t</sup>)(CO)<sub>3</sub>Cl molecular catalyst junction under CO<sub>2</sub> with varying monochromatic light (661 nm) intensity. (*Inset*) Cyclic voltammograms of Re(bipy-Bu<sup>t</sup>)(CO)<sub>3</sub>Cl under CO<sub>2</sub> and Ar atmospheres on hydrogen-terminated p-Si photocathodes (blue) and Pt electrodes (red).

between the semiconductor and redox species) is given by Equation 7 (116):

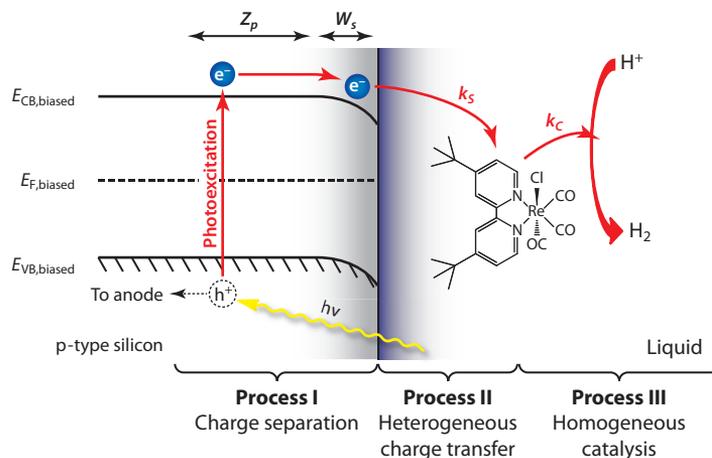
$$J_{total} = eQ \left[ 1 - \frac{e^{(-\alpha W_S)}}{1 + \alpha Z_p} \right] + en_0 \left( \frac{D_n}{Z_p} \right). \quad (7)$$

In this equation,  $Q$  is the photon flux,  $\alpha$  the absorption coefficient,  $W_S$  the depletion width,  $D_n$  the diffusion coefficient of the electron in the semiconductor,  $n_0$  the equilibrium concentration of electrons, and  $Z_p$  the electron diffusion length in the semiconductor.

Limiting catalytic current density for homogeneous catalysis with EC'-type mechanism is given by Equation 8 (85, 117, 118):

$$J_{\infty} = nFC_0^*(Dk'C_Z^*)^{1/2}. \quad (8)$$

In this equation,  $n$  is the number of electrons involved in the reduction (2 for CO<sub>2</sub> reduction to CO),  $F$  the faradaic constant,  $C_0^*$  the catalyst concentration,  $D$  the diffusion coefficient of catalyst,  $k'$  the catalytic rate constant, and  $C_Z^*$  the substrate concentration (CO<sub>2</sub> concentration). Equation 8 is derived for a quiescent solution with the assumption that the substrate concentration



**Figure 8**

A schematic of  $\text{CO}_2$  photoreduction by a p-type semiconductor/molecular junction with p-Si and a  $\text{Re}(\text{bipy-Bu}^t)(\text{CO})_3\text{Cl}$  molecular electrocatalyst junction as an example. The figure shows three processes involved in photoreduction of  $\text{CO}_2$  by a p-type semiconductor/molecular catalyst junction.

is higher than the catalyst concentration and that there is fast charge transfer between the electrode and molecular catalyst.

From Equations 7 and 8, it is clear that for a given p-type semiconductor/molecular electrocatalyst junction, the photocurrent density depends on incoming light intensity, whereas the limiting catalytic current density depends on catalyst concentration. To maximize photocatalytic current density, the photocurrent density and limiting catalytic current must be closely matched. Therefore, for a given semiconductor/molecular electrocatalyst junction, the catalyst concentration must be chosen corresponding to the illumination intensity used and the catalyst's TOF.

Based on the expressions for efficiency (see **Supplemental Section 1**), it is evident that the overpotential of  $\text{CO}_2$  photoelectrochemical reduction is usually unfavorable. A molecular catalyst with low or no overpotential for  $\text{CO}_2$  reduction and high TOF would be essential for direct conversion of light energy to chemical energy. However, most of the molecular catalysts with high TOFs also have high overpotentials (1, 4) (**Figure 4**). The integrated maximum photocurrent under Air Mass 1.5 illumination using the conventional Shockley–Quiesser limit for solar energy conversion for p-Si (1.12 eV), p-InP (1.3 eV), p-GaAs (1.4 eV), and p-GaP (2.3 eV) are  $44.0 \text{ mA cm}^{-2}$ ,  $37.0 \text{ mA cm}^{-2}$ ,  $32.5 \text{ mA cm}^{-2}$  and  $9.0 \text{ mA cm}^{-2}$ , respectively (78). Therefore, for low band gap semiconductors, obtaining high photocurrent densities requires the use of a molecular catalyst with high TOFs. Given Equation 8, it is also possible to increase the limiting catalytic current density for a given molecular catalyst by increasing its concentration. In this case, however, two issues arise: higher catalyst concentration will lead to an increase in light absorption by the solution, and the solubility of the catalyst is limited in any given solvent. Possible improvement in conversion efficiency can be achieved by using multijunction electrodes, which is proposed and discussed later in this review.

Supplemental Material

### 4.3. Heterogeneous $\text{CO}_2$ Photoreduction by Molecular Catalysts Anchored to the Semiconductor Surface

On account of competing advantages of homogeneous catalysts (selectivity, tunability) and heterogeneous catalysts (robustness, easy separation of products from catalysts), there is considerable

interest in “heterogenizing” homogeneous catalysts, by covalently linking them to surfaces. There have been several reports regarding surface modification of dark electrodes using the polymeric form of the molecular catalysts and/or enzymes for electrochemical reduction of CO<sub>2</sub> to various products (4, 44, 119–134). These modified dark electrodes have several advantages: control over the active site environment for better performance (119, 135); prevention of aggregation or dimerization of the molecular catalyst, which leads to higher TONs (136); efficient charge transfer to the molecular catalyst; usability of water-insoluble molecular catalysts in aqueous media once anchored to electrodes (137); and stabilization of the catalyst and electrode (138–141). The physical nature of these junctions is similar to a semiconductor/liquid junction with unbound molecular electrocatalysts (142). Molecular catalyst surface-modified semiconductors can be subdivided into two categories: polymeric backbone attachment, and direct anchoring to the semiconductor surface.

Aurian-Blajeni et al. (46) reported CO<sub>2</sub> photoreduction on polyaniline-coated p-Si at –1.0 V versus SCE in aqueous solution. In this report, formic acid and formaldehyde were formed with a FE of 20–30% after bulk electrolysis performed at –1.9 V versus SCE, with power conversion efficiency (see **Supplemental Section 1**) of 3–4%. Cabrera & Abruña (44) reported CO<sub>2</sub> photoreduction to CO by an electropolymerized molecular catalyst (Re(CO)<sub>3</sub>(4-vinyl,4'-methyl-2,2'-bipyridine)Cl) on p-Si and p-WSe<sub>2</sub>. A lower TON of 450 was reported compared with electropolymerized molecular catalyst on a metal surface (600 for surface-modified Pt) with FE of 100%. No calculations for conversion efficiency were made, as no information was provided about the illumination intensity for these systems.

Arai et al. (45) reported CO<sub>2</sub> photoreduction to formate in an aqueous medium by a p-InP/ruthenium-complex polymer junction. The ruthenium-complex polymer (RCP) used was [Ru(L-L)(CO)<sub>2</sub>]<sub>n</sub> (L-L = diimine ligand), which was previously reported as an electropolymerized catalyst (L-6) on Pt and vitreous carbon electrodes (127). CO<sub>2</sub> photoreduction was achieved at a potential –800 mV less negative versus glassy carbon/RCP (45). The best FE (63%) for formate production was obtained for a p-InP/RCP junction prepared by a two-step polymerization of RCP (127), which stabilized the polymeric film when under a cathodic bias (127) and in aqueous media (45). Low FE was reported in the above case due to competing H<sub>2</sub>- and CO-generation processes. No supporting electrolyte was added, which can result in high cell resistance and resistive losses.

Unlike dark electrodes, there are not many reports of semiconductor photocathodes modified with polymeric films. This could be due to the absorption of incoming light as well as a high number of photogenerated-carrier-trapping sites in the polymeric films.

To the best of our knowledge, there are no reports of photoelectrochemical CO<sub>2</sub> reduction by molecular catalysts directly attached to semiconductor surfaces. Recently, however, CO<sub>2</sub> reduction by molecular electrocatalysts/enzymes attached to semiconductor surface has been reported (143–146). Two of these report photocatalytic reduction of CO<sub>2</sub> to formate (144) or CO (145). Both systems are analogous to homogeneous photocatalytic reduction of CO<sub>2</sub> by photosensitizers and molecular catalysts discussed in Section 2. In the above cases, the molecular catalyst is either adsorbed or electrostatically attached to the semiconductor surface. A recent theoretical study (146) has shown covalent bond formation between Re(CO)<sub>3</sub>Cl(dcbpy) (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) and the TiO<sub>2</sub> rutile (001) surface but failed to recognize that Re(CO)<sub>3</sub>Cl(dcbpy) has no catalytic activity for CO<sub>2</sub> reduction (87).

Substantially more effort in molecular catalysts covalently bound to semiconductor surfaces is needed, with special consideration given to the accessibility of the catalytic site and its structural/activity requirements. The large cathodic bias required for photoelectrochemical reduction of CO<sub>2</sub> can cause adsorbed or electrostatically attached molecular catalysts to become loosened

from the semiconductor surface. Therefore, well-designed covalent attachment of the catalyst is imperative for stability of this method.

## 5. PROSPECT

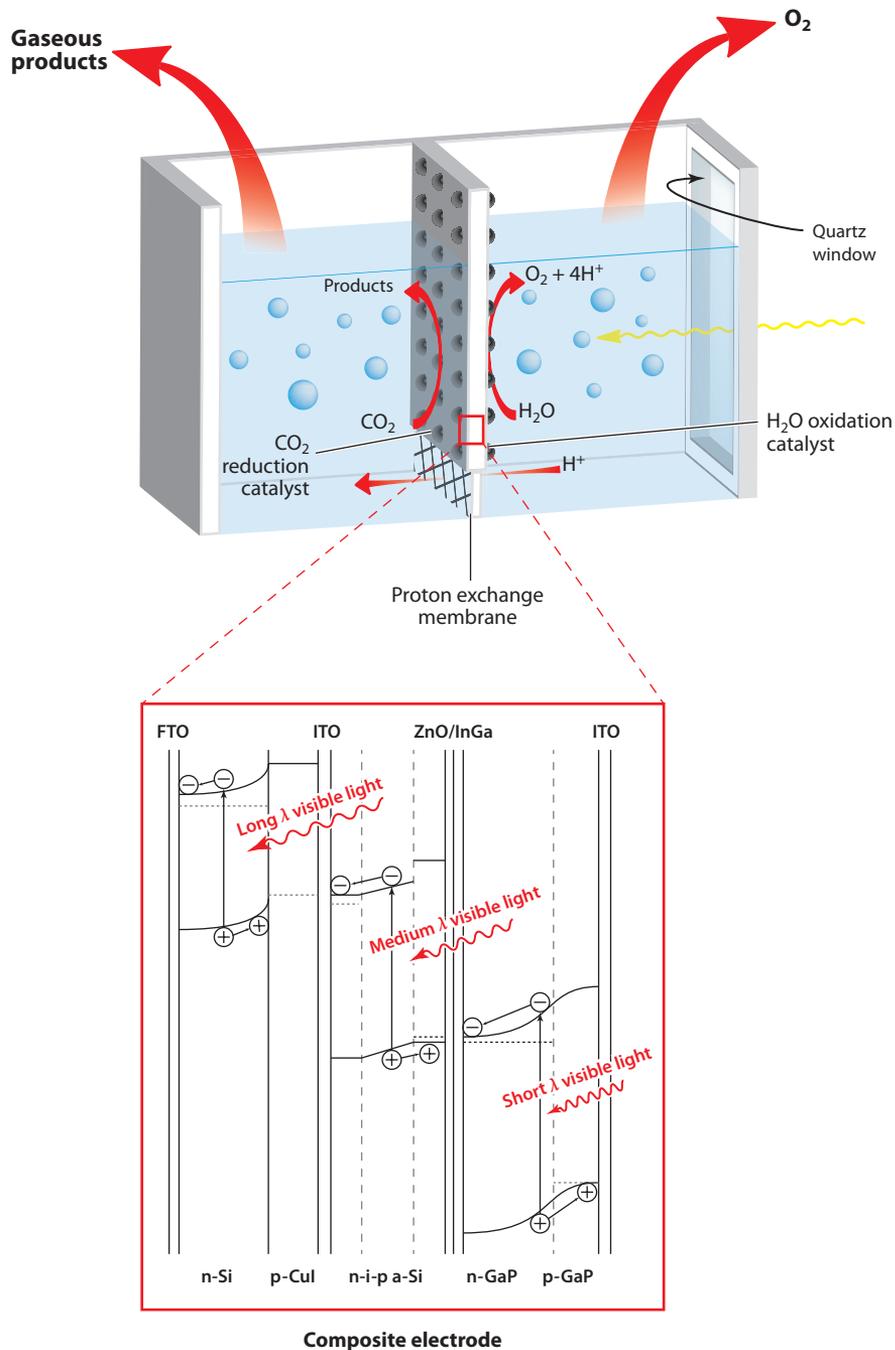
Multijunction photoelectrolysis cells are presently used to overcome the high potential that is associated with water splitting. Four types of these cells are currently used: p/n junction photoelectrolysis cells, photoanode-PV cells, photocathode-PV cells, and PV photoelectrolysis cells (147–150). An excellent analysis of these cells is presented by Walter et al. (78) in their review on solar water splitting. Similar efforts for CO<sub>2</sub> photoreduction are lacking.

Of note, the PV photoelectrolysis cell has a photovoltage that is independent of pH, which is important for pH-sensitive catalyst-mediated CO<sub>2</sub> reduction. This cell can also be easily modified with CO<sub>2</sub> reduction catalysts selective for specific products. In addition, this type of cell utilizes a majority of the solar spectra and has a high photovoltage, unlike wide band gap semiconductor photoelectrodes. The total thermodynamic potential to reduce CO<sub>2</sub> to products like CH<sub>3</sub>OH or CH<sub>4</sub> and to oxidize water to oxygen is only approximately 1.2 V. In practice, however, the applied potential required for simultaneous reduction of CO<sub>2</sub> and oxidation of water is at least 2.0 V. Water oxidation using PV electrodes has been explored by Yamane et al. (150). Photovoltages of 2.2 V and 1.7 V were reported with n-Si/p-CuI/ITO/n-i-p a-Si/n-p GaP/ITO/RuO<sub>2</sub> and n-i-p a-Si/n-p GaP/ITO/RuO<sub>2</sub>, respectively, with 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH = 6.3) as the supporting electrolyte.

It is possible for this technology to be used as a wireless, monolithic, two-compartment PV-type photoelectrolysis cell with single dual face photoelectrode. A proposed cell using a CO<sub>2</sub> reduction catalyst/FTO/n-Si/p-CuI/ITO/n-i-p a-Si/n-p GaP/ITO/water-oxidation catalyst electrode configuration is shown in **Figure 9**. The fabrication cost of the electrode may be high; however, the simple structure of the cell, the ease of product separation, and the robustness of the electrode could lead to a long operation time and an environmentally friendly process. There are two major challenges for these types of cells: identifying catalysts based on earth-abundant materials that have low overpotentials for CO<sub>2</sub> reduction and water oxidation, and finding a reliable and robust proton-exchange membrane. It is clear that the advantages of this type of system outweigh the cost. Therefore, it is imperative to explore and adopt water-splitting/hydrogen-generation technology for solar splitting of CO<sub>2</sub> for liquid fuel applications as well as to broaden the search for new robust, selective, and efficient catalytic systems. In the quest for new catalysts, combinatorial approaches will prove useful for both discovery and optimization of new catalysts (151).

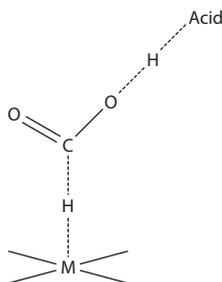
## 6. EXPERIMENTAL AND THEORETICAL CHALLENGES

Virtually every approach under consideration for the photochemical or photoelectrochemical reduction of CO<sub>2</sub> to fuels requires catalysts to facilitate the formation and cleavage of chemical bonds. In general, the required catalysts fall into three classifications: (a) They already exist and work but are too rare/costly to be scaled up; (b) they already exist but in forms that are not optimal or practical for adaptation to an integrated solar fuels system; (c) they do not exist and await discovery. The challenges in catalysis are large indeed. The best photovoltaic or photoelectrochemical materials can sustain current densities of 10–20 mA cm<sup>-2</sup>. In contrast, for a two-electron process, a monolayer of catalyst with a TOF of 1,000 s<sup>-1</sup> will sustain a current density of only 0.1 mA cm<sup>-2</sup>. Presently, no electrocatalysts for the reduction of CO<sub>2</sub> function at low overpotential with high selectivity, and hence would be useful for a large-scale system. The work reviewed here on the photochemical and photoelectrochemical reduction of CO<sub>2</sub> illustrates many of the difficult issues



**Figure 9**

Schematic of a proposed photochemical cell with a multijunction tandem photoelectrode for CO<sub>2</sub> photoreduction. The electrode structure is adapted from Yamane et al. (150). Abbreviations: FTO, fluorine-doped tin oxide; ITO, indium tin oxide.



**Figure 10**

Example of CO<sub>2</sub> activation by M-H and an acidic proton to produce formic acid.

in CO<sub>2</sub> reduction chemistry. How does one obtain a metal center that is sufficiently nucleophilic to bind CO<sub>2</sub> at low potentials (avoiding negative oxidation states like Re(-1), for example)? Can this be done with earth-abundant metals? The most costly thermodynamic issue appears to be CO<sub>2</sub> binding to the metal center. The most costly kinetic issue appears to be C-O bond breaking in the metal-CO<sub>2</sub> complex. There is evidence that Lewis acid cocatalysts can be used to accelerate CO<sub>2</sub> reduction catalysis, but the thermodynamic issue of a highly negative reduction potential remains.

Future experimental and theoretical work needs to examine whether catalysts that find low-energy transition states for CO<sub>2</sub> reduction are viable. Groups that stabilize negative charge on the CO<sub>2</sub> O-atoms should lessen the metal nucleophilicity requirement of the metal center and could also lower the barrier for C-O bond breaking. How much these factors can increase the efficiency of the CO<sub>2</sub> reduction catalysts needs to be determined, followed by the question of whether the oxidation state and reduction potential need to be as negative as they are for many of the systems reported. This may be done by computing CO<sub>2</sub> affinities for a variety of mid- to late-transition metal complexes for which the reduction potential and metal nucleophilicity can be varied by ligand substitution. The theory will need to be tested by experiment, and new complexes will need to be prepared to refine predictive abilities. From both thermodynamic and kinetic points of view, PCET mechanisms for CO<sub>2</sub> reduction appear to be more efficient. In some PCETs to CO<sub>2</sub>, it is a nucleophilic metal hydride and not the nucleophilic metal itself that engages CO<sub>2</sub> (**Figure 10**). Of course, this transition state produces formic acid, and if more reduced species such as methanol are desired, then the H donor/acceptor properties required to reduce formic acid also need to be identified.

Hydricities have now been measured for many transition metal (152) and NADH-like (153) hydride donors, and they have been applied to explain the thermodynamics of proton reduction catalysis. Hydricities have only recently been applied to CO<sub>2</sub> reduction (154). The expanding database of hydricities should be combined with theoretical studies of transition states for different types of CO<sub>2</sub> reduction to bring a more rational set of design principles to the problem of CO<sub>2</sub> reduction catalysis.

Theoretical approaches to understanding the energy landscapes of intermediates formed in the electrochemical reduction of CO<sub>2</sub> on copper surfaces have become available recently (107) This work is providing a clearer understanding of the potential dependence of the thermodynamic stability of key intermediates in the electrochemical reduction of CO<sub>2</sub>, and thereby the potential dependence of branching ratios for CO<sub>2</sub> reduction to different products. It appears that computational approaches to the kinetic barriers to key intermediates in the electrochemical reduction of CO<sub>2</sub> at other metal and semiconducting surfaces will also become available. One particularly

promising approach to photochemical and photoelectrochemical reduction of CO<sub>2</sub> in the future will be to address the kinetic and thermodynamic stability of the rate-limiting CO<sub>2</sub> reduction intermediates on electrode surfaces with molecular catalysts selected to accelerate the reduction of those intermediates.

## DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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