

Solar Air-to-Fuel Technologies for a Circular Carbon Economy

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ABSTRACT: The CO₂ present in our atmosphere is a universally available and abundant carbon feedstock, but it exists only in dilute concentrations (currently around 427 ppm). Clean technologies capable of capturing atmospheric CO₂ using direct air capture and directly converting it into synthetic fuels and chemicals using solar energy could pave the way for a circular chemical industry. Challenges in developing such a solar-powered air-to-fuel technology that mimics photosynthesis include the use of the low CO₂ concentration in air, the thermodynamic stability of CO₂ (and its capture products), the high O₂ content (21%) in air (which often interferes with catalytic CO₂ valorization), and the presence of variable moisture levels. This perspective explores different concepts and emerging technologies for the solar-powered conversion of atmospheric CO₂ into fuels and chemicals, examines their scientific principles, considers their scalability, and offers recommendations for future research to support the development of a net-zero circular carbon economy.

1. INTRODUCTION

Earth's natural carbon cycle plays a crucial role in sustaining life on our planet. Until the industrial revolution, the atmospheric carbon dioxide (CO₂) levels had largely remained stable (at below 300 ppm) for several thousand years, with forests, soil, and oceans sequestering nearly equal amounts of CO₂ to those being released by the natural processes (Figure 1).^{1,2} Since the industrialization of our planet over the past 250 years, vast quantities of additional CO₂ have been and continue to be released into the atmosphere by using the planet's fossil fuel reserves to meet the energy demands of our civilization.³ This additional anthropogenic CO₂ emission (currently at 30–40 billion tons per year) is causing a carbon cycle imbalance. Consequently, atmospheric CO₂ levels continue to rise, and while its effects in the form of global warming, climate change, ecological destabilization, ocean acidification, and others have long been predicted, they are now beginning to have a profound impact on our planet.^{4–7}

To address this, significant attention is being devoted to reducing net CO₂ emissions on a global scale.⁸ In devising future solutions, it is essential to recognize our reliance on carbon; as all life is composed of carbon, our economy runs on carbon, and our everyday materials largely depend on carbon. Anthropogenic carbon circularity can be achieved through a nature-inspired approach, where we develop efficient ways to capture and manipulate CO₂ from the air for everyday fuel and chemical synthesis.^{9,10} This air-to-fuel approach will not only enable us to recycle or reduce atmospheric CO₂ but also minimize our reliance on fossilized carbon.^{11–14} Aerobic utilization of CO₂ to produce fuels enables an anthropogenic net-zero carbon cycle, where CO₂ is reemitted into the atmosphere when the recycled fuel is used, closing the loop. Alternatively, aerobic CO₂ fixation into long-lasting chemicals, such as polymers, yields a carbon-negative cycle but is constrained by the limited amount of polymer required in human society.^{15,16} Another related carbon-

negative approach is the capture and subsequent storage of atmospheric CO₂ in geological formations, as in direct air carbon capture and storage (DACCS); however, the safety, prudence, and economic viability of storing gigatons of pressurized CO₂ underground remain the subject of considerable debate.^{17–20}

Among the ways to harness and chemically valorize CO₂ directly from air, the direct solar-powered route is ambitious but arguably the most promising long-term solution due to the abundance and the low cost of solar energy.^{21,22} As in natural photosynthesis, solar-powered air-to-fuel technologies aim to produce energy-rich carbon-based fuels directly from atmospheric CO₂, utilizing sunlight as the energy source (Figure 1).^{23–25} This approach offers several benefits: (i) it utilizes atmospheric CO₂ directly instead of relying on localized concentrated streams, (ii) it employs sunlight as a clean, emission-free, and abundant energy source,²⁶ and (iii) it creates value by synthesizing targeted fuels and chemicals tailored to our needs instead of solely storing CO₂ in the ground,²⁷ as envisaged by conventional DACCS.^{19,20} Considerations regarding the required efficiency and scalability make solar air-to-fuel conversion a formidable challenge. While nature has been carrying out this process for millions of years using photosynthetic organisms,²⁸ artificial systems for the process have only recently been explored and are at an early formative stage. These recent developments will be covered in this perspective.

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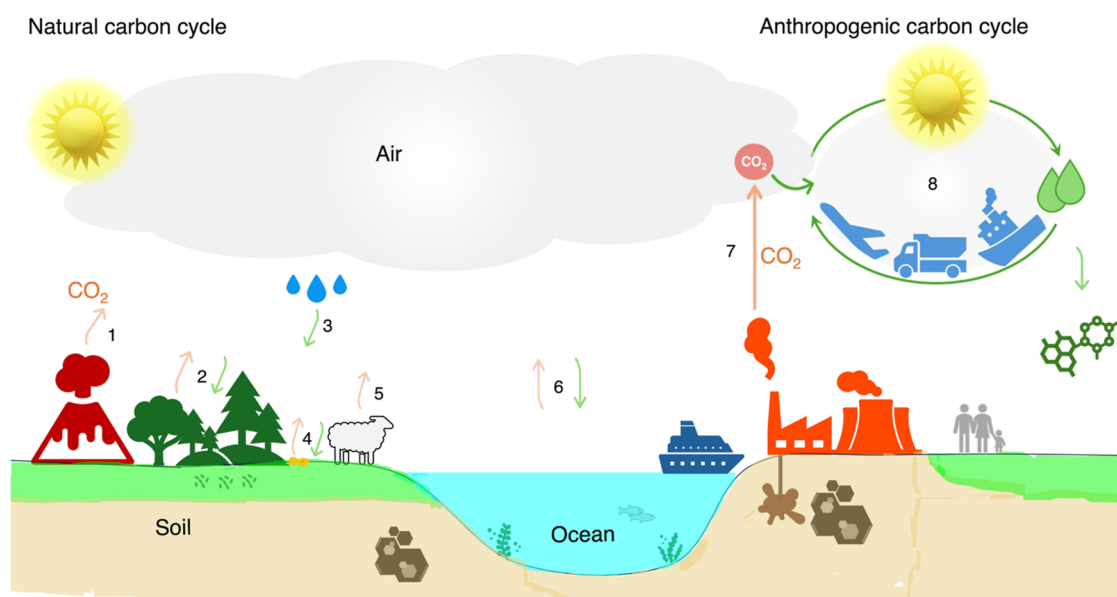


Figure 1. The net zero carbon cycle of the future. The natural circular carbon cycle is illustrated on the left, showing different carbon fluxes to and from air (nonexhaustive), including those from natural activities (1), forests (2), rainfall (3), topsoil (4), animals (5), and oceans (6). All natural fluxes combine to a total CO_2 emission of around zero. Flux 7 represents the anthropogenic CO_2 emission that currently enters the air without removal. The top-right corner illustrates the envisioned anthropogenic circular carbon cycle (8) through solar CO_2 recycling into fuels from air for a circular carbon economy.

2. CHALLENGES

2.1. Ultradilute CO_2 Concentration

One key challenge in working with atmospheric CO_2 is its low concentration in air, currently around 427 ppm (Figure 2a). Thermodynamically, it requires approximately $19.2 \text{ kJ mol}^{-1}_{\text{CO}_2}$, corresponding to $0.44 \text{ GJ ton}^{-1}_{\text{CO}_2}$, to concentrate ambient CO_2 from atmospheric levels to pure CO_2 at 1 bar (at temperature 25°C), which most solar utilization technologies would use as feedstock to avoid slow reaction kinetics arising from otherwise low substrate availability and slow mass transport (Figure 2b). Taking into account suitable kinetics, heat losses, efficiency losses, and the energy needed for air intake, current direct air capture (DAC) systems consume in reality between 5 and $9 \text{ GJ ton}^{-1}_{\text{CO}_2}$.²⁹ The majority of DAC technologies operate through chemical CO_2 capture, where CO_2 is first captured (absorbed or adsorbed) chemically and then extracted as a concentrated stream using a temperature or pressure swing.³⁰ The low CO_2 concentration in air necessitates capturing agents with high CO_2 fixation rates (lowest activation energy) for suitable kinetics that are often associated with greater thermodynamic stability of the captured CO_2 (Figure 2b), making subsequent release energy-intensive. Typical DAC materials utilize ethanolamines, specialized amines, or hydroxide-based agents as the active components,^{30,31} with extensive material development ongoing to create improved energy-efficient DAC chemical systems with faster reaction kinetics and lower thermodynamic energy penalty.^{32–35}

Beyond thermal processes, innovative DAC methods powered by alternative energy sources are also being explored. These include hybrid electrochemical DAC systems with electrochemically active redox species for reversible CO_2 capture,^{36–38} electrochemically mediated amine regeneration techniques via the competitive binding of a redox-active metal ion with amines,^{39–42} moisture swing DAC adsorbents for regeneration through a humidity alteration in the feed gas,^{43–45} electrochemically or photochemically triggered pH swings for

reversible CO_2 capture and release,^{46–49} and membrane-based CO_2 separation from air.^{50,51} Comprehensive analyses of these systems have recently been undertaken.^{52–54} These emerging technologies are in early stages and require further development before they can be used in DAC facilities.

CO_2 from air can also be used directly for conversion without prior concentration to avoid the DAC energy penalty, but the low CO_2 concentration makes the reaction kinetics in such systems sluggish.⁵⁵ This is often exacerbated by interference from other high-concentration reactive species in the air such as oxygen and moisture.

2.2. High Oxygen (O_2) Content

The O_2 concentration in the atmosphere is 21%, approximately 500 times that of CO_2 . Unlike the most abundant and mostly inert gas in the atmosphere, nitrogen (N_2 ; 79%), O_2 is a reactive diradical that can interfere with the CO_2 conversion process. The facile nature of the oxygen reduction reaction is reflected in its positive and thus favorable reduction potential (to OH^- , H_2O_2 , or H_2O), compared to CO_2 reduction reactions.⁵⁷ Nature has addressed this problem in photosynthesis by developing the ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) enzyme, which is several orders ($\sim 10^3$) more active in reducing CO_2 than O_2 (Figure 2c).^{58,59} Several factors, including high active-site affinity, enhanced local solubility, and stabilizing side-chain interactions, contribute to RuBisCO's preference for reducing CO_2 over O_2 , which nature has refined over millions of years.^{60,61} Even so, for plants lacking a local CO_2 concentration mechanism where CO_2 is uptaken through the leaf stomate and directly relayed to RuBisCO in mesophyll cells (C3 plants), RuBisCO is known to reduce, on average, one O_2 molecule (photorespiration, hence the term oxygenase in its name) for every three molecules of CO_2 (photosynthesis), reducing the overall photosynthesis efficiency by approximately 25% (Figure 2d).^{62,63}

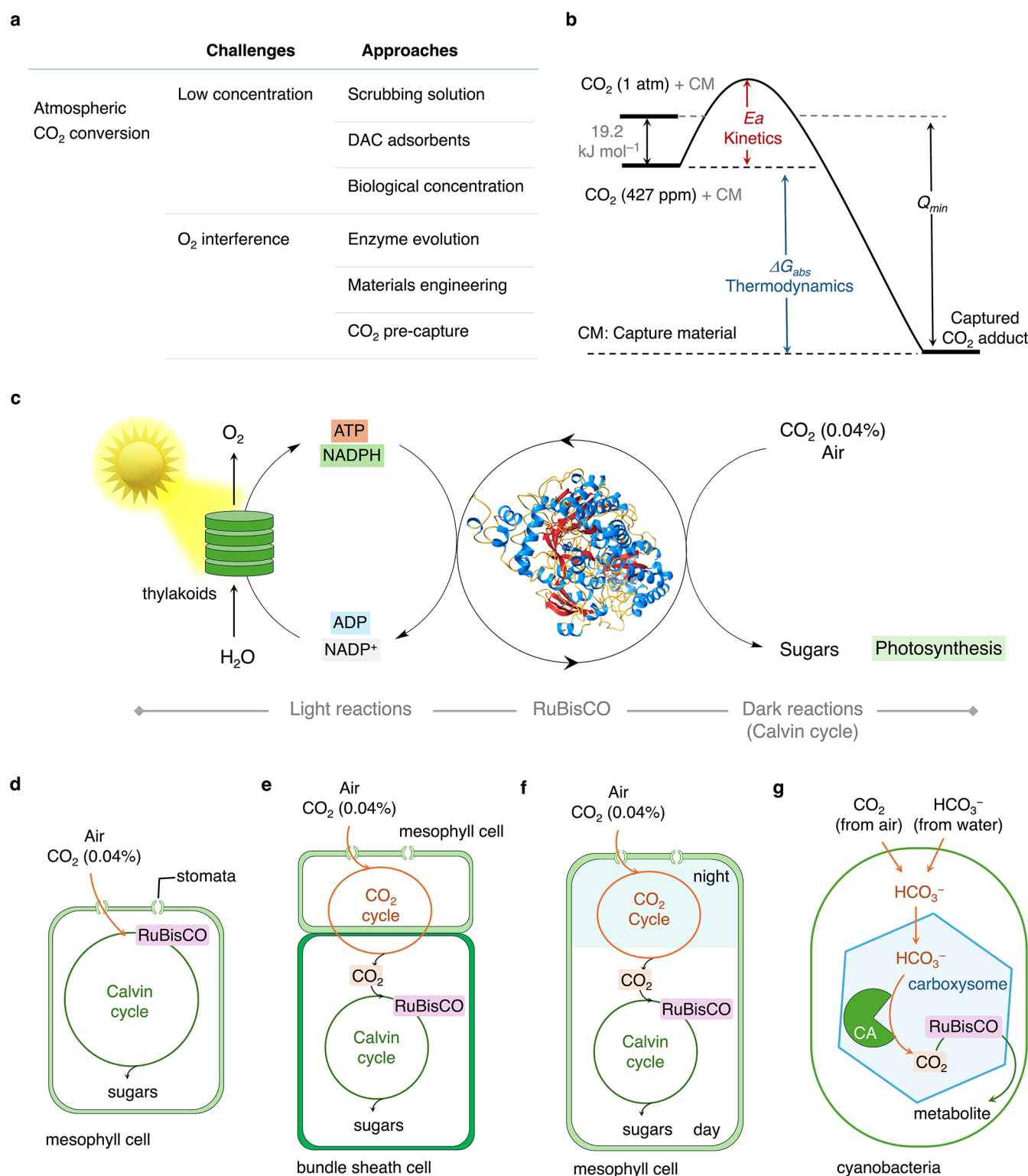


Figure 2. Challenges in CO₂ reduction from air and nature's solutions. (a) The challenges and various approaches, (b) the thermodynamic and kinetic considerations (E_a , ΔG_{abs} , and Q_{min} refer to the activation energy, free energy change during CO₂ absorption, and minimum work for release to 1 atm CO₂, respectively), and (c) natural atmospheric CO₂ fixation during photosynthesis enabled by the RuBisCO enzyme. The RuBisCO structure is taken from the National Institutes of Health database and is available in the public domain.⁵⁶ (d–g) Various CO₂-relaying and concentrating mechanisms observed in nature to deliver atmospheric CO₂ to RuBisCO, including in C3 plants (d), C4 plants (e), CAM plants (f), and cyanobacteria (g) (CA denotes carbonic anhydrase).

2.3. Nature's CO₂ Concentrating Mechanisms

Selectivity for CO₂ reduction is enhanced in nature through a preconcentration mechanism in C4 plants, where atmospheric

CO₂ is initially fixed as part of a four-carbon compound within mesophyll cells and then released in the bundle sheath cells at higher concentrations around RuBisCO, where the Calvin cycle

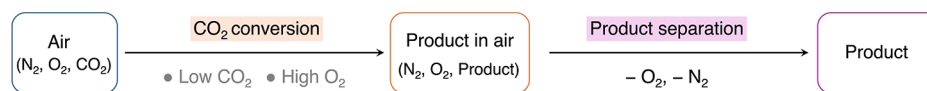
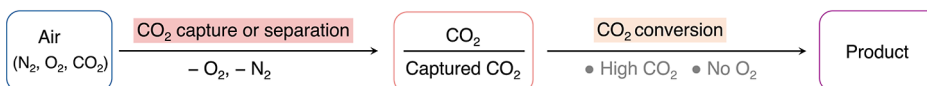
Direct CO₂ conversionStepwise CO₂ conversion

Figure 3. Direct and stepwise air capture and conversion. The direct route consists of direct CO₂ conversion at low CO₂ concentrations in the presence of O₂. In the stepwise approach, CO₂ is first captured or separated from N₂ and O₂, followed by its conversion.

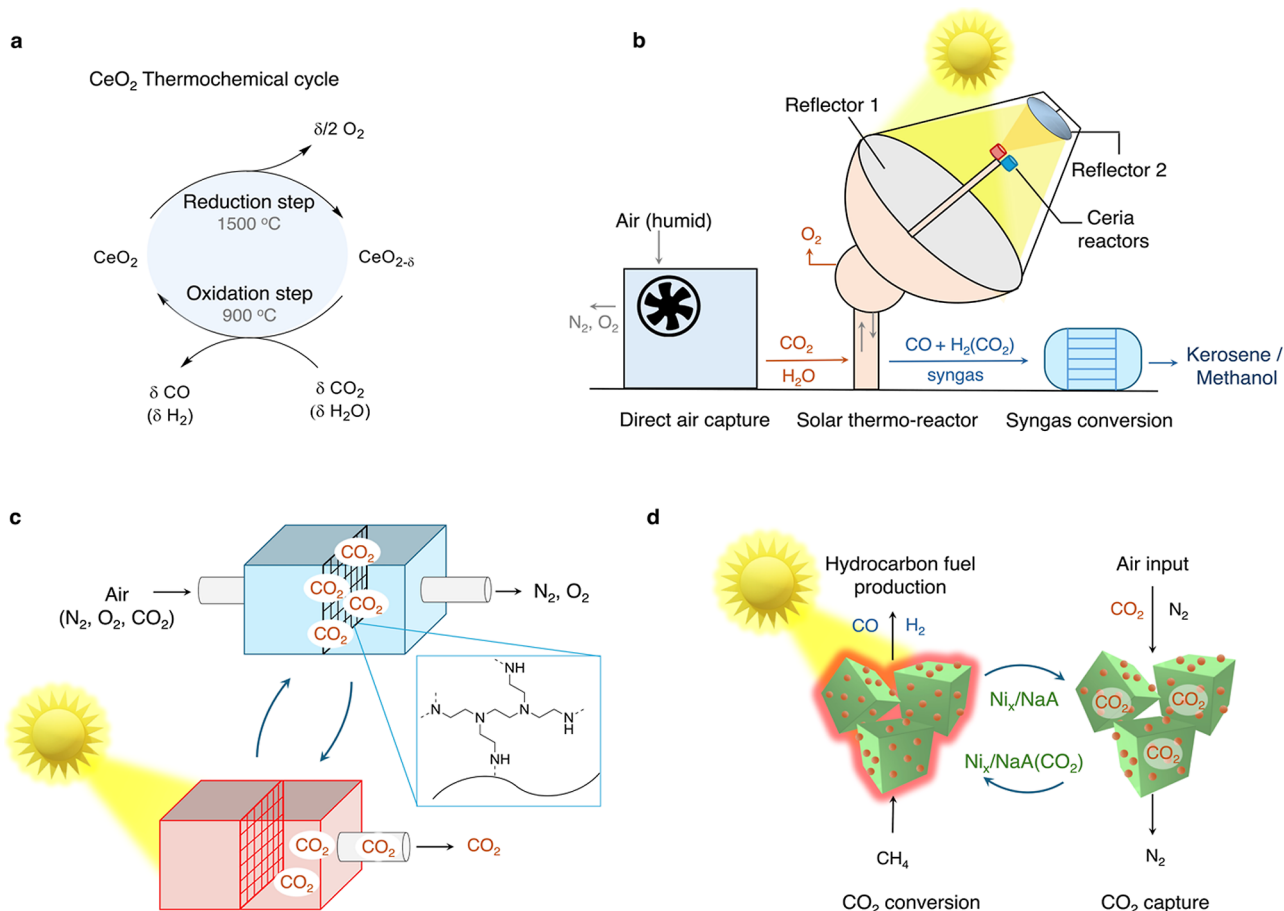


Figure 4. Solar-thermal air-to-fuel systems. (a) CeO₂-based thermochemical cycle, (b) the solar-thermal air-to-fuel technology with three distinct steps⁸⁹ (the red and blue ceria reactors represent the “hot” (1500 °C) and “cold” (900 °C) chambers, respectively), (c) the direct air capture system using immobilized amines,⁹⁰ and (d) solar-thermal air-to-fuel technology using dual functional materials for CO₂ capture and conversion.⁹⁷

(dark reactions) takes place (Figure 2e).^{64,65} Alternate ways to improve CO₂ reduction selectivity, as seen in nature, include temporal separation of CO₂ uptake and reduction, as in CAM (Crassulacean Acid Metabolism) plants, where CO₂ is stored overnight and released for reduction during the day (Figure 2f),^{66,67} or the local release of concentrated CO₂ via pH swing within microcompartments called carboxysomes found in cyanobacteria. Carboxysomes contain the enzymes carbonic anhydrase and RuBisCO close to each other, where carbonic anhydrase facilitates the local concentrated CO₂ release, and RuBisCO fixes the released CO₂ in situ (Figure 2g).^{68,69} Devising synthetic methods to achieve a similar competitive

advantage in CO₂ reduction in the presence of 21% O₂ has proved challenging, with prominent approaches being surface hydrophobic treatment, catalytic molecular tuning, and introduction of CO₂ transport relays to active sites, among others.^{57,70–72}

2.4. Temporal Decoupling of Capture and Reduction

A nature-inspired strategy to avoid O₂ interference has been the temporal decoupling of the CO₂ capture and conversion processes into separate steps, as in CAM plants, rather than simultaneous capture and conversion (Figure 3).^{73,74} The common chemicals used in CO₂ capture (including DAC), such as amines, ethanolamines, and hydroxides, are unreactive toward

nonelectrophilic O_2 . Thus, CO_2 can be selectively separated and captured in the solution by these chemicals while allowing other gases, such as N_2 and O_2 , to pass through. The CO_2 -loaded solution can then release pure CO_2 gas using solar power. Such a decoupled system can operate throughout the full diurnal cycle, using night-time to concentrate aerobic CO_2 in solution and day-time for the release and conversion of pure CO_2 .⁷⁵

2.5. Presence of Moisture and Other Impurities

Complications can arise from the presence of moisture in air, which fluctuates throughout the diurnal cycle. For physisorbing DAC materials based on porous, ordered structures (zeolites, metal–organic frameworks), humidity can substantially reduce their CO_2 capture performance due to competitive binding within the pores.⁷⁶ Conversely, chemisorbing DAC materials (especially amine-based ones) exhibit improved CO_2 capture rates and capacities in humid conditions, but coadsorption of water increases the energy intensity of desorption while decreasing the purity and recovery rate of CO_2 .^{77–79} The presence of moisture in the recovered CO_2 can further interfere with its downstream conversion, often necessitating additional CO_2 drying or moisture-stabilizing steps. In addition, in many electro- and photo-catalytic CO_2 utilization processes, some moisture is required to supply the protons needed for the CO_2 -reduction chemistry to proceed.

Besides O_2 and moisture, other impurities present in air, such as NO_x and SO_x , can potentially interfere with DAC or conversion, but their aerobic concentration is typically low enough (parts per billion levels) to avoid any prominent effect. This contrasts with CO_2 capture and utilization from dilute industry sources such as postcombustion flue gases where elevated SO_x and NO_x levels are commonly observed (100–1000 ppm).^{72,80}

3. STATUS

Several innovations have been reported recently for the direct synthesis of fuels and chemicals from atmospheric CO_2 , with sunlight serving as the primary energy source. These technologies utilize various approaches, including physical, chemical, and biological CO_2 fixation, combined with thermochemical, electrochemical, photochemical, and biochemical conversion pathways to achieve solar air-to-fuel synthesis, as detailed below.

3.1. The Solar–Thermochemical Pathway

3.1.1. Thermochemical Looping. CO_2 can be split into CO and O_2 at high temperatures via a thermochemical cycle using oxygen-transport materials, such as ceria (CeO_2) (Figure 4a).^{81,82} CeO_2 , when treated at high temperatures (above 1000 °C), releases O_2 from its structure to form reduced oxygen-vacant ceria ($CeO_{2-\delta}$, δ up to 0.04). Reduced CeO_2 , when exposed to CO_2 or H_2O at a lower temperature (<1000 °C), extracts oxygen from these feedstocks to fill its oxygen vacancy while producing carbon monoxide (CO) and hydrogen (H_2), respectively. Besides CeO_2 , other oxygen-transport materials can also be used to split H_2O and CO_2 at high temperatures, including zinc oxide, metal-doped iron oxides, iron–aluminum oxides, and perovskite materials.^{83–87} The material must maintain a stable lattice structure at the required high temperatures (~1500 °C) under repeated heating and cooling cycles for a prolonged period to be effective for continuous operation. The process can be solar-driven when concentrated sunlight is used to achieve high temperatures. When sunlight is used directly to heat the transport material, it is termed direct

thermochemical splitting. Conversely, if concentrated solar heat is transferred via a heat-transfer liquid, it is termed an indirect process.⁸⁸

Most high-temperature CO_2 splitting reports based on thermochemical looping using oxygen-transport materials have focused on using prepurified concentrated CO_2 . Recently, Steinfeld and co-workers have demonstrated its integration with direct air CO_2 capture to produce drop-in fuels from sunlight and air (Figure 4b).⁸⁹ In the first step, CO_2 and moisture are captured from the air using well-established solid amine-based adsorbents developed by the same group in the early 2010s (now pursued through the spin-off company Climeworks).^{90,91} These adsorbents release captured CO_2 at moderate temperatures (80–100 °C) or under reduced pressures (Figure 4c). In the developed technology, air-captured CO_2 is released under mild heat (100 °C, obtained from waste heat of the solar refinery, vide infra) at reduced pressure (<0.1 bar) and fed to a solar refinery at ambient pressure, where the second step, conversion to syngas (a mixture of CO and H_2 , which is an industrial fuel and chemical precursor), takes place.

The solar refinery employs porous CeO_2 blocks, which are initially heated to 1500 °C using highly concentrated solar light (intensities of up to 3000–5000 kW m^{−2}, equivalent to 3000–5000 suns) via a parabolic dish collector (Figure 4b).⁹² This step, also known as the reduction or oxygen-release step, is performed under reduced pressure (0.1 mbar) to maximize oxygen vacancies in reduced ceria. In the subsequent oxidation or oxygen-uptake step, concentrated sunlight is moved away from the block, allowing it to cool down. Air-captured CO_2 and H_2O are then introduced at ambient pressure, around 900 °C, to complete the thermochemical cycle by restoring the oxygen atoms to ceria while producing syngas (Figure 4a). The porosity of the ceria block plays a crucial role and is tuned to balance two opposing factors: an increase in solar absorption with larger pore sizes, and an increase in reaction rate with smaller pore sizes due to an increase in the surface area of the block.^{88,93} The regenerated CeO_2 is reused in the next thermochemical cycle.

This process can produce approximately 4 L of syngas per kilogram of CeO_2 per cycle, demonstrated for a few hundred cycles, with a recorded solar-to-syngas efficiency of around 3–5%.⁸⁹ The produced syngas can be utilized to produce liquid fuels in a downstream gas-to-liquid (GTL) unit, such as to methanol (marine fuel) using an industrially established Cu/ZnO/ Al_2O_3 syngas-to-methanol catalyst or to kerosene (aviation fuel) via Fischer–Tropsch synthesis.⁸⁹ The GTL conversions are typically conducted at around 200–300 °C by using waste heat from the solar refinery, making the process entirely solar-driven. The overall system efficiency of this air-to-fuel process was estimated to be around 1%. It has been scaled to 50 kW (~50 m² of solar irradiance) at IMDEA Energy in Spain for CO_2 -to-fuel production, albeit without the DAC component, and material stability over long reaction times poses a challenge.⁹⁴ Other challenges include high capital expenditure requirements (for heliostat field), need for large amounts of porous CeO_2 (critical mineral) and quartz, high radiative heat loss during operation, nonstoichiometric oxygen transfer, and material sintering at elevated temperatures, which reduce efficiency and longevity.^{95,96}

3.1.2. Solar Thermal Catalysis Using Dual Sorbent Materials. Besides thermochemical looping, dual-functional catalytic sorbents can also be used for DAC and its subsequent conversion to synthesis gas under concentrated sunlight (Figure 4d), as reported recently by Liu and co-workers.⁹⁷ Unlike the

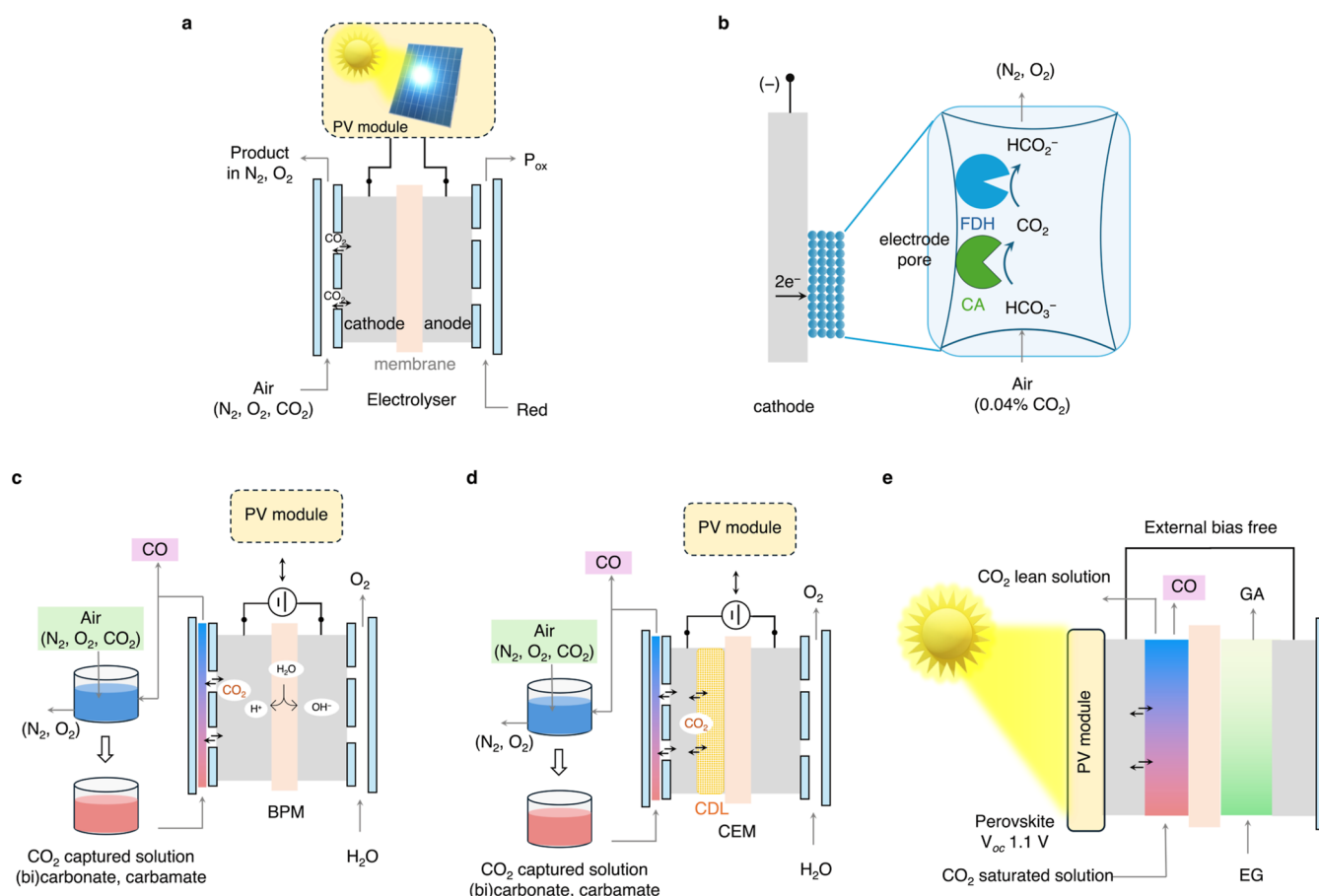


Figure 5. Photovoltaic-driven electrochemical air-to-fuel systems. (a) Photovoltaic (PV)-driven electrolysis directly from air (Red denotes the reductant, P_{ox} denotes the oxidized product), (b) carboxysome-inspired semiartificial approach where carbonic anhydrase (CA) converts bicarbonate to CO_2 for formate dehydrogenase (FDH) inside electrode pores to produce formate from air,¹⁰⁷ (c) stepwise approach for electrolysis of air-captured CO_2 solutions using bipolar membranes (BPM) for local CO_2 release,^{74,108} (d) direct carbonate or carbamate electrolysis with a CO_2 diffusion layer (CDL) for CO_2 transport to the cathode¹⁰⁹ (CEM denotes the cation exchange membrane), and (e) the buried junction photoelectrochemical system operating directly by sunlight under external bias-free conditions⁷³ (V_{oc} , EG, and GA denote the open-circuit voltage, ethylene glycol, and glycolic acid, respectively).

thermochemical looping systems, where CO_2 capture and utilization occur at separate locations with different materials, here the sorbent plays roles in both CO_2 capture and conversion. The adsorbent consists of a commercial zeolite, NaA, which aids in CO_2 capture, and is impregnated with nickel, which facilitates CO_2 conversion. In a typical reaction setup, a CO_2 -containing gas (including simulated air) is first passed through the adsorbent at ambient temperature for preloading of CO_2 (up to around 1 mmol per gram of the adsorbent). The adsorbent is then exposed to concentrated sunlight (around 410 sun intensity, 410.2 kW m^{-2}) under CH_4 flow, resulting in adsorbed CO_2 release and its conversion to synthesis gas via dry methane reforming process with reaction temperatures reaching 700°C under concentrated light illumination. CO_2 conversion of up to 95% is reported under these conditions. However, using the same material as both the capture sorbent and the conversion catalyst limits the scale of the single-cycle reaction due to limited CO_2 adsorption. Continuous switching between capture and conversion required for continuous operation can also be challenging.

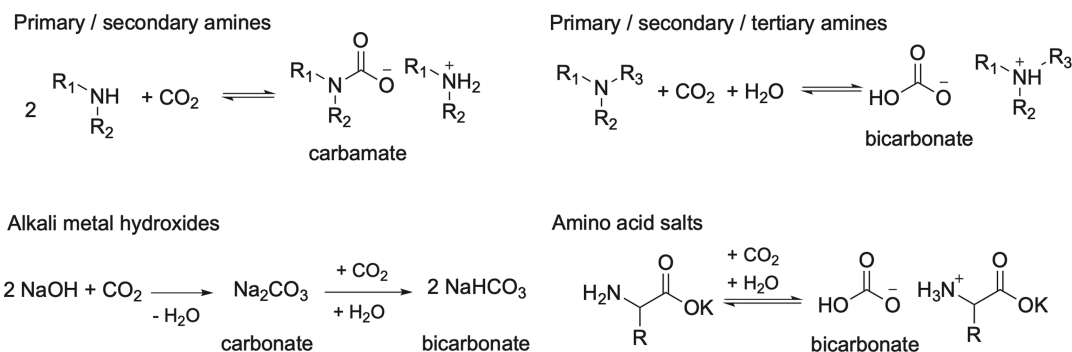
3.2. The Photovoltaic-Driven Electrochemical Pathway

CO_2 can also be recycled into fuels and chemicals using electrical energy, with or without the aid of high temperatures.^{98,99} High-

temperature (typically operating above 500°C) solid oxide electrolysis cells (SOECs) have been intensively investigated for CO_2 -to-fuel conversion and have been reviewed recently.^{100–102}

The integration of SOECs with DAC systems has recently been envisioned.¹⁰³ This process can be solar-driven if the required electricity and heat are generated with photovoltaic panels and concentrated solar thermal power, respectively. Electrochemical systems can also reduce CO_2 without high temperatures and, consequently, without the thermodynamic Carnot losses. The reduction of pure CO_2 using near-ambient-temperature electrolyzers has advanced rapidly in recent years, with current densities reaching $A \text{ cm}^{-2}$ levels.^{104–106} However, the electrochemical conversion of CO_2 directly from air remains challenging due to low CO_2 and high O_2 concentrations (Figure 5a).

3.2.1. Electrochemical Systems without Photovoltaic Integration. **3.2.1.1. Direct Electroreduction from Atmospheric Concentration CO_2 .** We have recently reported a nature-inspired approach for CO_2 capture and electroreduction from atmospheric concentrations, utilizing a local carbon-concentration mechanism involving carboxysome-type microconfined structures, as found naturally in cyanobacteria (Figure 2g). Similar to cyanobacteria, where carbonic anhydrase (CA) and RuBisCO are colocalized within a carboxysome, we immobilized carbonic anhydrase and the CO_2 reductase formate dehydrogen-

Scheme 1. CO₂ Capture by Different Chemicals with the Chemical Species Formed

ase (FDH) enzymes next to each other within the pores of a mesoporous indium–tin oxide (ITO) electrode (Figure 5b).¹⁰⁷ During electrolysis in pH ranges 7–8, CA facilitates the local release of gaseous CO₂ from dissolved bicarbonate, which is then consumed by FDH as a substrate to produce formate. This strategy to maximize the local CO₂ concentration is particularly promising for low atmospheric CO₂ concentrations due to the linear Michaelis–Menten-type kinetics observed with enzymes under low substrate conditions, resulting in a 4–8-fold increase in FDH activity for formate production.¹¹⁰ A >90% Faradaic efficiency for formate production at –0.6 V vs the standard hydrogen electrode (SHE) was observed, but the current density was low (~60 μA cm⁻²). Further, the system is oxygen-sensitive due to the observed oxygen reduction reaction under aerobic conditions, a major challenge for direct aerobic CO₂ reduction.¹¹¹

3.2.1.2. Electroreduction of Chemically Captured Aerobic CO₂. A promising alternative to direct CO₂ electroreduction from air involves capturing the aerobic CO₂ in solution first, followed by its electrolysis (Figure 5c).^{72,112,113} Chemical carbon capture using active chemical agents, such as amines, metal hydroxides, and amino acid salts, is an effective method for storing CO₂ in solution while separating it from O₂ and N₂ (Scheme 1 and Figure 3). The Sargent group reported an electrolyzer system that can directly reduce carbonate electrolyte into synthesis gas, using silver-based catalysts.⁷⁴ This approach used a bipolar membrane-based electrolyzer where membrane-generated local protons during electrolysis migrated to the cathode, resulting in local CO₂ release from carbonate with subsequent reduction (Figure 5c). Following this strategy, syngas at a 3:1 H₂/CO ratio was produced by direct carbonate electrolysis without any gaseous CO₂ contamination, achieving current densities of 150 mA cm⁻² (energy efficiency ~30%). However, the required cell potential was high (3.8 V) due to the use of a bipolar membrane and the thermodynamic stability of carbonate salts, and no carbon conversion efficiency (yield of CO produced from CO₂ supplied) was reported (vide infra for a note on carbon efficiency on captured CO₂ electrolysis). The cell voltage can be reduced slightly (~3.3 V at 100 mA cm⁻²) by replacing the bipolar membrane with a cation exchange membrane (CEM) and using a composite CO₂ diffusion layer (CDL) between the cathode and CEM to facilitate CO₂ transport from the membrane to the cathode (Figure 5d).¹⁰⁹

Along similar lines, Breugelmans and co-workers reported a bipolar membrane-based zero-gap flow electrolyzer for the electroreduction of direct air-captured (bi)carbonate solutions into formate or CO using tin oxide or silver nanoparticle-dispersed carbon electrodes (SnO₂/C or Ag/C, respectively).¹¹⁴

Current densities of around 50 mA cm⁻² were observed at a cell voltage of around 3.5 V, with Faradaic efficiencies for formate or CO production of around 15%. In addition to one-carbon products, multicarbon products such as ethylene can be produced by bipolar membrane-based carbonate electrolysis systems using copper–silver electrodes,¹⁰⁸ where silver facilitates CO₂ to CO conversion, and copper induces multicarbon product formation from CO-type intermediates.^{115–118} At a cell voltage of 3.8 V, a carbonate-to-ethylene Faradaic efficiency of 10% was achieved with a carbonate-to-ethylene conversion efficiency of 0.002–0.003%. Besides silver-based catalysts, a copper and cobalt phthalocyanine (CoPc) composite catalyst (Cu/CoPc-CNT, CNT being carbon nanotubes) deposited on carbon paper has also been demonstrated for efficient C₂ product formation from carbonate solution electrolysis, with ethylene and ethanol being the main observed products.¹¹⁹

Given that alkali (bi)carbonate is one of the most stable chemical species formed via CO₂ capture, alternative amino-acid-based electrolytes have also been developed for the capture and direct electrochemical reduction of atmospheric CO₂.¹²⁰ These systems employ amino acids with basic side chains, such as lysine, arginine, or deprotonated amino acids, such as potassium glycinate (Scheme 1), to capture aerobic CO₂, followed by the electrochemical reduction of captured CO₂ using a Zeolitic Imidazolium Framework (ZIF)-8 based nickel single-atom catalyst. Instead of a bipolar membrane, the reported electrolyzer used a simple cation-exchange membrane, producing CO from captured CO₂ with >50% Faradaic efficiency at a cell voltage of around 3 V and consuming about 30% less energy than alkali hydroxide-based systems.¹²⁰ Apart from the electrochemical, electro-thermochemical hybrid devices are also reported for CO₂ concentration and conversion to CH₄ from air, albeit without solar integration.¹²¹

The carbon conversion efficiency, defined as the fraction of starting CO₂/(bi)carbonate molecules converted to reduction products (CO, C₂H₄, etc.), is an important but often overlooked parameter in direct (bi)carbonate/carbamate electrolysis.¹²² The few studies reporting carbon conversion efficiency indicate that only traces of captured carbon are converted to fuel. The difficulty in carbonate reduction increases with increasing carbon conversion (when the base is regenerated as part of the reaction) as in situ release of gaseous CO₂ from the remaining carbonate-depleting electrolyte becomes increasingly difficult.^{73,108} Consequently, currents, voltages, and energy and Faradaic efficiencies are expected to falter significantly during the course of the reaction when the carbon conversion efficiency increases, which is of industrial relevance and has not yet been

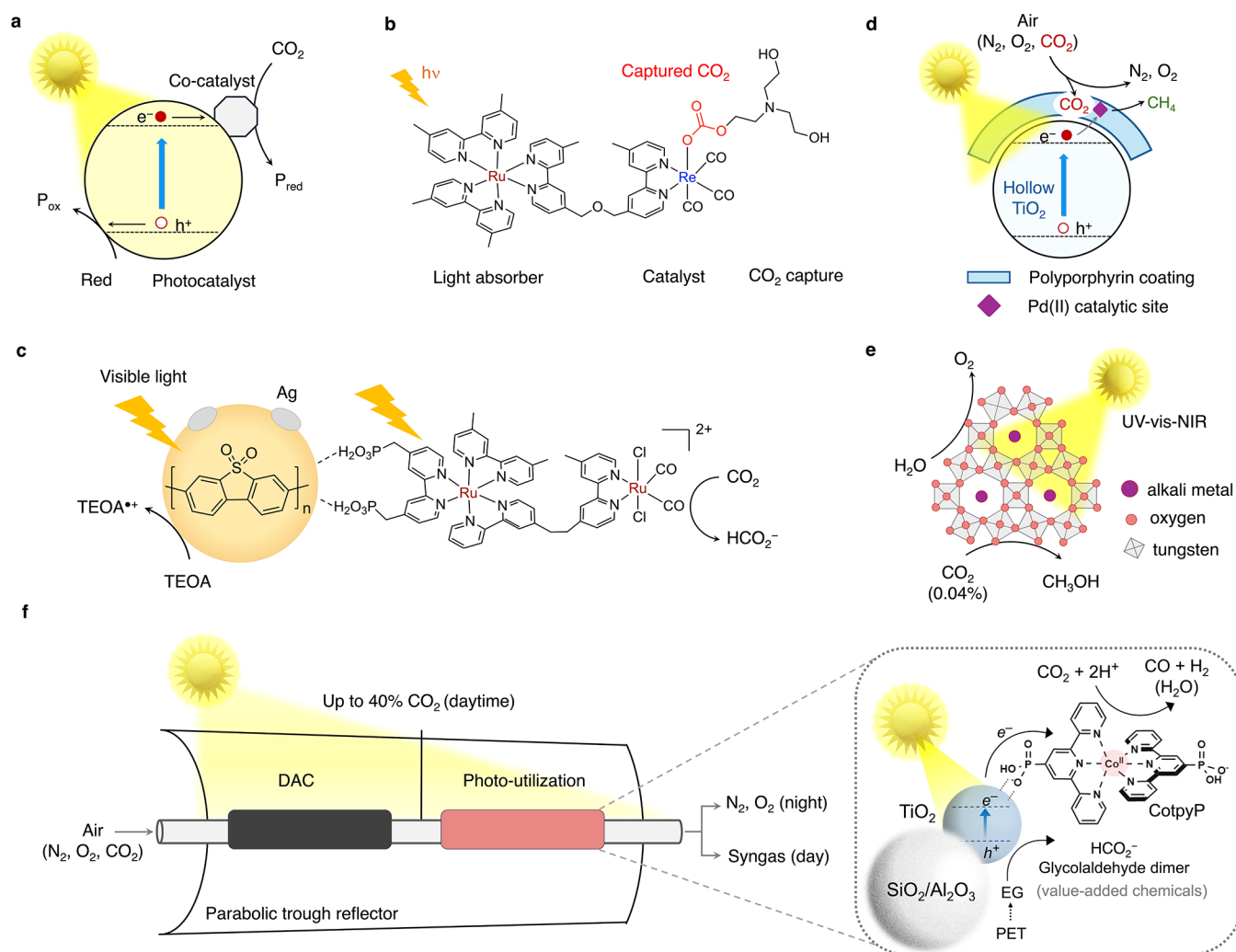


Figure 6. Photochemical solar air-to-fuel technologies. (a) Schematics of photochemical CO_2 reduction (Red, P_{red} and P_{ox} denote the reductant, reduction products, and oxidation products, respectively), (b) an example of a bimolecular complex for photochemical CO_2 conversion from dilute streams,¹³³ (c) extended molecular conjugates for photochemical CO_2 reduction to near quantitative yield using polymer-based visible light absorbers¹³⁴ (TEOA denotes triethanolamine), (d) strategy to enhance local CO_2 concentration and ward off O_2 through transparent polyporphyrin coating with embedded Pd(II) catalytic centers,¹³⁵ (e) CO_2 reduction from air using face selective hexagonal tungsten bronze materials,¹³⁶ and (f) the dual-bed direct air CO_2 capture and utilization technology developed by us for solar air-to-fuel synthesis⁷⁵ (DAC: direct air capture, PET: polyethylene terephthalate, EG: ethylene glycol).

sufficiently addressed. Similar issues persist in photocatalytic CO_2 reduction, where catalytic activities are typically reported but CO_2 conversion efficiencies are commonly overlooked (vide infra, Section 3.3).^{123,124}

3.2.2. Electrochemical Systems with Demonstrated Photovoltaic Integration. Although the above-mentioned electrolyzers can, in principle, be integrated with photovoltaic-driven renewable electricity generation, this has not been specifically demonstrated. The required cell voltages for these processes (3–4 V) are too high to be efficiently generated by a single light absorber using incident sunlight, necessitating multijunction or multiple solar cells. For example, if integrated with state-of-the-art commercial silicon solar cells (providing open-circuit voltages of 0.6–0.7 V), it will require 4–5 cells connected in series to operate the electrolyzer with incident sunlight, which can make it area-intensive and inefficient. The required cell voltage can be reduced by moving from the thermodynamically demanding water oxidation ($E^0 = -1.23$ V) as the counter-anodic reaction to waste-derived alcohol oxidation. The waste oxidation reactions can include the

oxidation of glycerol from biodiesel production, ethylene glycol sourced from polyethylene terephthalate (PET) plastic waste, glucose from biomass, or many other waste sources and typically have standard oxidation potentials close to zero ($E^0 \sim 0$ V).¹²⁵

By employing this strategy and utilizing ethylene glycol from PET waste oxidation as the counter reaction, we have shown that aerobic CO_2 can be captured and converted to syngas using even a single perovskite-based light absorber with an open-circuit voltage of 1.1 V (Figure 5e).⁷⁵ The CO_2 from the air is captured with a KOH solution dissolved in ethylene glycol and then used directly as an electrolyte in the next conversion step. The solar-driven reduction is performed using a buried-junction photocathode fabricated by integrating a perovskite solar cell with a cobalt phthalocyanine CO_2 -reduction catalyst deposited on multiwalled carbon nanotubes. When immersed in the air-captured CO_2 solution electrolyte and irradiated with sunlight, the buried junction photocathode produced syngas without any externally applied bias for over 100 h at current densities of around $\sim 0.1 \text{ mA cm}^{-2}$, albeit with a relatively high H_2/CO ratio (20–25) while selectively oxidizing ethylene glycol to glycolic

acid at the anode in a two compartment H-cell separated by a bipolar membrane. For other dilute CO₂ sources, such as simulated postcombustion flue gas with ~15% CO₂ concentration, a higher Faradaic efficiency for CO production (~20%) and higher current densities (~1–2 mA cm⁻²) were observed. The carbon conversion efficiency of the process was below 1%.

3.3. The Direct Photochemical Pathway

CO₂ can also be converted into fuels and chemicals using sunlight in a direct photochemical process, without requiring electrode wiring.¹²⁶ In direct photochemical processes, sunlight is captured by a light absorber (molecular or material-based) to generate an electron–hole pair. The electron is then transferred to CO₂, often facilitated by a cocatalyst, to produce CO₂-reduction products, while the hole is transferred to a reductant (electron donor) to complete the redox process (Figure 6a).¹²⁷ Adequate bandgap alignment and interfacing between the photosensitizer, catalysts, and substrates are necessary to enable vectorial electron and hole transfer in opposing directions to minimize recombination losses. This is often achieved by bandgap and interface engineering through various methods, including doping, structural modifications, alloying, strain engineering, heterojunction formation, cocatalyst modifications, and others.^{128–130} Simultaneously, the choice of the cocatalyst influences product selectivity, which also, to some degree, depends on the reaction medium. The photocatalytic reduction of CO₂ using sunlight has been reviewed recently.¹²⁶ Most photocatalytic CO₂ reduction processes operate under concentrated 100% CO₂ conditions to ensure high substrate availability without oxygen. Direct photochemical CO₂ reduction from air is considerably more challenging due to low ambient CO₂ concentration and oxygen interference.^{55,131,132}

3.3.1. CO₂ Photoreduction from Dilute Concentrations in Anaerobic Concentrations. Ishitani and co-workers (and others) have designed molecular complexes through additive and coordination sphere engineering for CO₂ photoconversion from dilute streams (including 0.04% CO₂) under anaerobic conditions via localized CO₂ capture.^{133,137} In these systems, a light absorber molecule (such as ruthenium tris(bipyridyl) (Ru(bpy)₃)) is typically conjugated with a CO₂ conversion catalyst (such as rhenium bipyridyl tris(carbonyl)), while the reaction is carried out with a CO₂ scavenger in the solution (such as triethanolamine) (Figure 6b).¹³³ When light is irradiated onto the solution, the light-absorbing moiety is photoexcited to generate a HOMO–LUMO (electron–hole) pair. Due to suitable alignment of the energy levels (verified in prior experiments), the electron moves to the catalyst, where CO₂ reduction takes place. Triethanolamine, present in solution, plays a dual role. First, it scavenges CO₂ from the solution to bring it near the catalytic center via Re–O(carbonate) bond formation, ensuring local CO₂ availability even at dilute concentrations. At the same time, triethanolamine also acts as a sacrificial electron donor (reductant), quenching the generated hole at the light absorber while being oxidized. Applying this chemical principle, the reduction of CO₂ from dilute streams with concentrations as low as 5000 ppm (diluted in argon) has been demonstrated. This corresponds to retaining 60% of the catalytic activity compared to catalysis in pure 100% CO₂, with a molecular turnover number of 150 after 5 h. A 480 nm wavelength monochromatic light was used, and the system is also active in an electrochemical setup.¹³⁸

The light absorption can be extended to a broader visible region by attaching the molecular structure further to an efficient conjugated polymer-based solar absorber, such as P10, the 10-unit-long homopolymer of dibenzo[*b,d*]thiophene sulfone.^{139,140} A recent report by Sprick and co-workers showed near-quantitative CO₂ conversion to formate under photocatalytic conditions using a similarly designed system at low CO₂ concentrations (with triethanolamine as the sacrificial electron donor), with a turnover number of around half a million under 460 nm light (Figure 6c).¹³⁴ Catalytic activity under low CO₂ concentrations is needed to achieve high CO₂ conversion in any catalytic system but is often overlooked in photocatalytic CO₂ reduction studies due to low conversion yields typically observed.¹⁴¹ Other reports on the developments of low-concentration CO₂ reduction using molecular systems have been reviewed recently.¹³⁷

It is worth noting that the molecular systems often require sacrificial electron donors (e.g., triethanolamine), which, although useful for catalytic studies to investigate the CO₂ reduction half-reaction at an early stage, are not practical for large-scale implementation due to their high cost and stoichiometric consumption/decomposition.¹⁴² Further, molecular systems, due to their well-defined HOMO–LUMO energy gap, often show narrow absorption bands in the solar spectrum (apart from the polymeric systems) that can limit overall efficiencies when using the full solar spectrum. The molecular systems described above are effective for photocatalytic low-concentration CO₂ reduction only under anaerobic conditions due to their sensitivity to oxygen.

3.3.2. CO₂ Photoreduction Directly from Air. Direct aerobic CO₂ photoconversion can be achieved by modifying local catalytic environments with specialized materials to increase the local CO₂ concentration (for improved rate kinetics and mass transport) and to ward off oxygen, favoring CO₂ reduction over O₂ reduction. This was attempted recently by the Wang group, who employed a composite photocatalyst consisting of a hollow TiO₂ core with surface-coated hypercross-linked porphyrin-based polymers coordinated to active Pd(II) sites (for CO₂ reduction) to achieve direct aerobic CO₂ photoconversion to CH₄ under ultraviolet–visible (UV–vis) light irradiation (Figure 6d).¹³⁵ Here, the TiO₂ generated electron–hole pairs upon light irradiation and also catalyzed water oxidation as the counter reaction on its surface. The surface-deposited porphyrin-based polymer ensured high CO₂ availability near the Pd(II) centers, by capturing CO₂ from air, with the Pd atoms serving as active catalytic centers for CH₄ formation. Employing this strategy, the authors reported a 12% conversion yield of CO₂ to CH₄ from air after 2 h of UV–vis irradiation (325–780 nm).¹³⁵

Along similar lines, Zhang, Zhao, Sun, and co-workers have reported a series of hexagonal tungsten bronze materials with the formula M_{0.33}WO₃ (M being alkali metals such as K, Rb, Cs) with exposed reactive {010} facets that are active in direct aerobic CO₂ reduction under UV–vis–NIR illumination (Figure 6e).¹³⁶ These materials were prepared solvothermally from tungsten hexacarbonyl (W(CO)₆) and metal nitrate precursors, among which Rb_{0.33}WO₃ showed the most activity in aerobic CO₂ photoreduction to methanol under full-spectrum radiation (350–2500 nm) or even selective near-infrared (NIR) irradiation (λ > 800 nm), producing methanol with 98% selectivity after 4 reaction hours and ~4% CO₂ conversion yield. Doping these structures with molybdenum (3–5%), specifically in Cs_{0.33}WO₃, can further enhance the catalytic activity several-

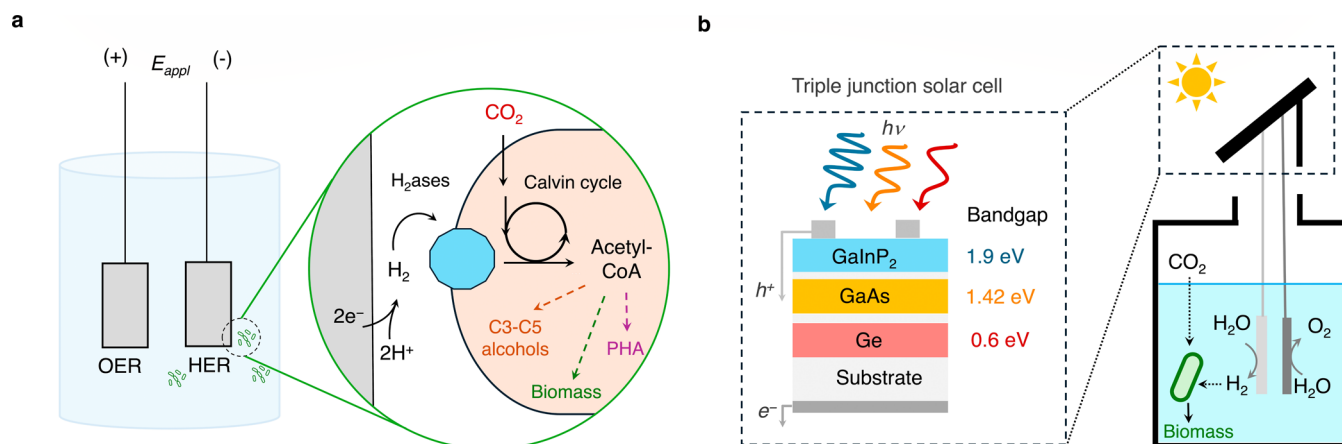


Figure 7. Inorganic–biological hybrid solar air-to-fuel technologies. (a) The electrochemical biohybrid setup for aerobic CO_2 reduction to C3–C5 alcohols under an electrochemical bias, with a shown biological CO_2 fixation pathway^{152,153} (OER, HER, and PHA denote the oxygen evolution reaction, hydrogen evolution reaction, and polyhydroxyalkanoate, respectively). (b) The photovoltaic integration of the biohybrid electrolysis setup using an external triple junction solar cell.¹⁵⁴

fold (3–4 $\times$) under anaerobic conditions.¹⁴³ Other structures, such as rose-like assembled bismuth oxychloride (BiOCl) nanosheets rich in bismuth vacancies with exposed active {001} facets, are also found to be active for CO_2 capture and photoconversion from air, with activities reaching around 20 $\mu\text{mol g}^{-1} \text{h}^{-1}$ for CO production under a UV–vis irradiation for 5 h.^{135,144,145}

A few notes on the challenges in aerobic CO_2 photoconversion and semiconductor photocatalysis in general are warranted here. First, the kinetic activities of these photocatalytic systems remain low due to high charge recombination rates. Consequently, the analyzed product amounts are often small and subject to large errors.^{146,147} In CO_2 photoreduction specifically, many products, such as CO and CH_4 , can also form from impurity photodegradation.¹⁴¹ Therefore, additional verification methods, including robust controls and isotope-labeling experiments, are necessary to identify CO_2 -derived products and calculate true catalytic rates.¹⁴⁸ This issue is particularly prominent in direct photocatalysis of aerobic CO_2 , where low CO_2 availability and high oxygen levels further promote the degradation of non- CO_2 carbon sources such as organics.⁷⁵

3.3.3. CO_2 Photoreduction Following Direct Air Capture. Besides direct photochemical CO_2 conversion from air, where the product is typically diluted in O_2 and N_2 (Figure 3), CO_2 can alternatively be precaptured in solution, followed by photoreduction. Han, Liu, and co-workers have shown that CO_2 from air can be precaptured using a task-specific ionic liquid consisting of a tetrabutylphosphonium cation and a pyridinium 2-oxide anion $[\text{P}_{4444}][\text{P}-2-\text{O}]$.¹⁴⁴ Along with atmospheric CO_2 , the ionic liquid also captures atmospheric moisture to form a bicarbonate species. The captured CO_2 (as bicarbonate) is directly reduced photocatalytically in the next step by using a pyrene-based conjugate polymer. A CO production rate of 47.37 $\mu\text{mol g}^{-1} \text{h}^{-1}$ was obtained under visible light irradiation using triethanolamine as the sacrificial electron donor, with around 98% selectivity for CO formation due to suppression of the H_2 evolution reaction in the ionic liquid medium.

When employing a localized capture (by amines, hydroxides, zeolites) near catalytic centers, it is worth noting that CO_2 in its captured state is thermodynamically more stable and kinetically more inert than free CO_2 . Thus, while in situ capture increases

local CO_2 concentrations (in the captured form), subsequent conversion is often challenging without prior CO_2 release.¹¹² Addressing this issue, we have designed a stepwise dual-bed direct air-to-fuel reactor that captures, concentrates, and converts CO_2 from air into CO in a sequential manner using sunlight (Figure 6f).⁷⁵

The photoreactor involves a transparent glass tube reactor with two separate fixed reaction beds—one for DAC and another for CO_2 photoutilization—mounted on a parabolic trough reflector for sunlight concentration (3–5 kW m^{-2} ; 3–5 sun) (Figure 6f). The upstream DAC bed contains a solid silica-amine adsorbent to capture CO_2 from air during nighttime ‘dark’ operation. During the day, solar light is concentrated onto the tube, heating the capture bed to temperatures exceeding 100 $^\circ\text{C}$ (a photothermal cover is used for efficient solar heating) and facilitating the release of air-captured CO_2 in a concentrated stream toward the downstream utilization chamber. Depending on the flow rate, CO_2 concentrations of more than a thousand times (of air) can be achieved (from 0.04% to >40% v/v). The downstream bed contains molecularly engineered titania nanoparticles with anchored phosphonated Co bis(terpyridine) CO_2 reduction catalysts supported on alumina or silica nanopowder (Figure 6f, right) that use concentrated sunlight to convert incident CO_2 to syngas. PET waste-derived ethylene glycol is presupplied to the conversion bed, which serves as the electron source (reductant), decreases overall energy demand, avoids explosive oxygen-fuel mixture formation, and is transformed into value-added products during the process (all of which may ultimately contribute to the practicality of this process). Although this nascent technology currently exhibits low solar-to-chemical efficiency, future improvements are anticipated, in terms of enhanced catalyst activity, stability, and solar absorption.

3.4. The Inorganic–Biological Hybrid Pathway

One primary reason artificial conversion of CO_2 from air has been challenging is its low ambient concentration, but nature has developed intricate biological mechanisms to address this challenge. Nature’s ability to fix aerobic CO_2 can be exploited to design a hybrid approach where biological organisms are employed for low-concentration aerobic CO_2 fixation (via reduction) and integrated with artificial chemical systems to provide the required energy (for example, via solar light

harvesting). Among biological organisms, *Cupriavidus necator* (formerly known as *Ralstonia eutropha*) is a soil bacterium with several intriguing capabilities. It can easily adapt between heterotrophic and autotrophic modes, meaning it can grow either by using other organic carbon sources (heterotrophic) or produce its own carbon-containing biomass from inorganic carbon, including atmospheric CO₂ (autotrophic). In its autotrophic mode, *C. necator* can utilize H₂ (through hydrogenase enzymes (H₂ases)) as an energy source to fix ambient CO₂ into biomass for its growth. Under nutrient-deficient conditions, the biomass formation pathway switches to a carbon-storing mechanism that synthesizes polyhydroxyalkanoate (PHA) at high concentrations instead of forming biomass.^{149,150} Perhaps most intriguingly, the PHA synthesis pathway following CO₂ fixation under nutrition-deficient conditions can be genetically engineered in this bacterium to produce targeted energy-rich carbon products, including fusel alcohols (C3–C5).¹⁵¹

3.4.1. Bioelectrochemistry without Solar Integration.

The genetically engineered *C. necator* bacterium's ability to fix atmospheric CO₂ into fusel alcohols using H₂ under nutrient-deficient conditions can be combined with H₂ production through solar water splitting to synthesize (C3–C5) bioalcohols from atmospheric CO₂ using sunlight, as demonstrated by Nocera, Silver, and colleagues.^{152–156} Their biohybrid technology, called the Bionic Leaf, merges biological CO₂ fixation with Nocera's previously developed artificial leaf technology for solar H₂ production,^{157,158} enabling solar-powered aerobic CO₂ conversion into liquid fuels (Figure 7a). A similar approach was previously explored by Liao and colleagues using genetically engineered *C. necator* for electrobiofuel (isobutanol) production, utilizing formic acid as an energy vector.¹⁵⁹

Initial reports on the Bionic Leaf focused on the electrochemical aspects, investigating the potential integration of these chemical and biological pathways via intermediate H₂ production.¹⁵³ Major innovations involved developing efficient water electrolysis systems that can operate under conditions conducive to bacterial growth, including a moderate pH (6–8) and low cell potentials (2–3 V). A self-healing cobalt phosphate (CoP_i) anode catalyst was found to be effective for catalyzing the oxygen evolution reaction at near-neutral pH, whereas a NiMoZn alloy was used as the cathode catalyst. The electrolyte consisted of CO₂-saturated phosphate buffer (pH 6.5–7.5; minimal medium) with an added culture of *C. necator* (wild-type or engineered). When this electrochemical cell was operated at a potential of nearly 2.7–3.0 V with wild-type *C. necator*, rapid bacterial biomass growth was observed by optical density analysis due to the consumption of the in situ generated H₂ by the bacteria. At lower potentials (<2.7 V), a loss in bacterial growth and activity was observed due to the formation of H₂O₂ and other reactive oxygen species (ROS). When operated at 3.0 V with a genetically engineered *C. necator* strain in the electrolyte specifically designed for targeted isopropanol synthesis, the selective formation of isopropanol via in situ CO₂ fixation and reduction was observed (Figure 7a). Isopropanol concentrations in the electrolyte reached 216 mg L⁻¹ after 5 days, with 90% carbon selectivity toward isopropanol (current densities around 5 mA cm⁻², cell voltage 3.0 V).

The required cell potential was later reduced to 2.2 V by using an alternative cathode comprising a cobalt phosphorus (Co–P) catalyst that minimized the formation of H₂O₂ and ROS at these low potentials.¹⁵² Furthermore, the Co–P cathode and CoP_i anode can work synergistically to minimize leached cobalt in the

electrolyte, enabling it to be transported to and deposited on the anode, leading to an increased cell viability. Using this approach, effective biological fixation of CO₂ from air (containing 400 ppm of CO₂) into biomass was demonstrated with wild-type *C. necator* at an overall electrochemical cell voltage of 2.0 V and at current densities of ~5 mA cm⁻², with an electricity-to-biomass efficiency of around 20%. Using genetically engineered *C. necator* strains, the product selectivity can be altered to produce C3 or C4 + C5 alcohols, with 25–40% energy efficiencies from pure CO₂.

3.4.2. Bioelectrochemical with Solar Integration. Low required cell potentials (≤2 V) also enable efficient integration of the biological–inorganic hybrid electrolyzers with solar photovoltaic cells (Figure 7b).¹⁵⁴ The required cell voltage was obtained from a triple-junction solar cell consisting of Ge, GeAs, and GeInP₂, with bandgaps of 0.6, 1.42, and 1.9 eV, respectively. The solar cell produced an open-circuit voltage of 2.4 V, with peak power observed near 2.0 V at a current density of ~10 mA cm⁻². The attached hybrid electrolyzer contained Co–P and CoP_i catalysts as the cathode and anode, respectively, with wild-type *C. necator* in the electrolyte medium for biological CO₂ fixation using in situ generated H₂. When no external voltage was applied, the integrated photovoltaic-driven biohybrid electrolyzer operated at a potential difference of approximately 2.3 V across the electrodes with a current density of 7 mA cm⁻², producing bacterial biomass from pure CO₂ with an energy (solar-to-chemical) efficiency of around 6.1%. The efficiency was lower than the achievable peak (~10%, photovoltaic efficiency × electrolyzer efficiency) due to a voltage mismatch between the solar cell output and the electrolyzer input. While this study focused primarily on the utilization of pure CO₂, activity for CO₂ fixation from the aerobic atmosphere can be expected based on previous reports. In addition to CO₂ fixation to biomass or carbon-based alcohols, the bacterium can be engineered to produce fine chemicals, including pharmaceuticals, or even fertilizer (NH₃) through N₂ fixation (bionic leaf-N).^{160–163}

4. DISCUSSION

Several approaches are thus being explored for solar air-to-fuel synthesis to enable future utilization of atmospheric CO₂. These technologies are at early stages, with technological readiness levels (TRLs) ranging from 2 to 5. Significant technological improvements, both in DAC and in solar-powered CO₂ conversion, along with their effective integration, are needed to make solar air-to-fuel technologies a market reality. Key features of representative examples of these technological approaches are summarized in Table 1.

Currently, the thermochemical pathway (Figure 4) is at tentative TRL values of 3–5. The core technology is being trialed by the spinout company Synhelion to produce solar aviation fuel at several thousand liters per year.¹⁶⁴ However, the CO₂ here is captured from concentrated biogenic emissions rather than air to improve economics. The cost of carbon capture increases significantly when transitioning to ultradilute sources such as air. Thus, any fuel produced via photothermal technology following DAC would be more expensive than current biogenic emission-derived fuels. Under optimistic scenarios, the price of synthetic aviation fuel from air-derived CO₂ produced by this technology is estimated at around \$2–\$5 per liter, compared to virgin fossil-based aviation fuels at <\$1 per liter.⁸⁹ Another recent study has reported a tentative price of air-

Table 1. Overview of Representative Solar Air-to-Fuel Technologies

Technological approach	CO ₂ capture method	Conversion technology	Operating temperature ranges	CO ₂ conversion	Products	Solar to fuel efficiency	Major efficiency loss	Major advantages	major concerns	tentative TRL ^a	ref
Solar-photothermal	Solid amine-based adsorbents	Thermochemical looping	900–1500 °C	20–40%	H ₂ (75–90%) ^b , CO (6–10%) (further to methanol or kerosene)	1–5%	Radiative heat loss	Mature solar thermal facilities	Area intensity, heat loss, CapEx ^f , critical materials	3–5	89
Photovoltaic-electrochemical	Aqueous hydroxide or amino acid solutions	Direct carbonate and carbamate electrolysis	RT ^h –80 °C	0–10%	H ₂ (50–90%) ^c , and CO (10–50%) or C ₂ H ₄ (5–12%) or HCO ₂ [−] (20–80%)	3–8% ^e	Electro-chemical overpotential and resistance	High area activity (for electrolysis)	High capex, cell stability, membrane prices, carbon conversion	3–4	108,109,114,120
Direct photochemical	Solid adsorbents/photocatalyst material	Solar catalysis using molecules or semiconductors	RT–100 °C	0–10%	H ₂ (20–30%) ^b , and CO (70–80%) or CH ₄ (>90%), or MeOH (>95%)	0.05–1%	Charge carrier recombination Low sunlight absorption	Low CapEx ^f High scalability	Low activity, material stability	2–3	75,135,136
Inorganic-biological hybrid	Biological CO ₂ fixation by C ₃ neocitor	(Photo)electrolysis with microbial CO ₂ conversion	RT–40 °C	90–100%	Liquid fuels (C3 or C4–C5) (55–70%), or biomass (30–45%)	3–6% ^{d,e}	Photovoltaic electrochemical integration PV efficiency	Biological inorganic integration	Scalability, reaction rate	3–4	152

^aTRL denotes the technology readiness level. ^bH₂ generated from coadsorbed moisture. ^cH₂ generated from aqueous solution. ^dAssuming a solar cell efficiency of 20%, coupled to the electrolyzer.

^eTentative efficiency for CO₂ conversion from air, efficiency higher for pure CO₂. ^fCapEx means Capital Expenditure. ^gPV denotes photovoltaic. ^hRT denotes room temperature.

derived methanol by this route at near \$8 per liter, markedly higher than its current market price (<\$1 per liter).¹⁶⁵

The prices can be reduced by increasing the overall solar-to-fuel efficiency of the system from its current 1% to 10%, particularly by optimizing the syngas production process in the solar refinery. This can be addressed by improving heat recovery as radiative heat loss is significant at high operating temperatures (1000–1500 °C) and is being explored as part of the European SUN-to-LIQUID II project.¹⁶⁶ Opportunities also lie in discovering alternative oxygen-transport materials that can facilitate the thermochemical cycle at lower temperatures,^{167,168} achievable in lower sunlight concentrations and, consequently, reducing radiative heat loss and area intensity (Figure 8). Efforts

Technological route	Possible directions
Concentrated solar thermal	Improved heat integration
	Lower temperature cycle
	Earth abundant materials
	Improved specific activity
PV-driven electrolysis	Better electrocatalyst design
	Electrolyte engineering
	Improved PV integration
	Alternative oxidation
Direct photochemical	Efficient light absorber
	Avoiding sacrificial reductants
	O ₂ -resistant material development
	Gas-phase photocatalysis
Inorganic-biological hybrid	Strain engineering for chemicals
	Improved abiotic-biotic integration
	Improved bacterial longevity
	Scale-up exploration

Figure 8. Future research directions among different technological routes.

are ongoing in this regard, focusing on doping ceria with other oxide materials. The use of earth-abundant, noncritical minerals would aid large-scale adoption, and iron-based oxides show promise, but their high-temperature passivation remains a challenge.^{169,170} The mature process of solar thermal electricity generation using concentrated solar power with steam turbines¹⁷¹ could help scale up this relatively new fuel generation technology, utilizing existing solar fields. Still, the need for high temperatures, large-area solar fields, high capital expenditure for solar concentrators, large amounts of ceria (a critical mineral), and low specific product yield (mass of product per unit mass of ceria per cycle) could persist as problems for the foreseeable future in the absence of any significant breakthroughs.

The photovoltaic-driven electrochemical pathway (Figure 5) does not suffer from significant radiative heat loss (operating at near-ambient temperatures) and is not limited by Carnot inefficiencies. However, the reported developments are still in the early stages. Direct photovoltaic-driven electrochemical reduction of aerobic CO₂ in solution is more challenging as it

combines the difficulty of low CO₂ concentration with its low solubility in water. Consequently, the initial capture of CO₂ in an electrolyte solution (using amines, hydroxides, etc), followed by photovoltaic-driven electrolysis, is likely a more manageable approach.^{172,173} The captured-CO₂ electrochemical reduction systems can achieve high current densities (0.1–0.5 A cm⁻² levels) and, consequently, high specific area activity. However, the low carbon conversion efficiencies and the high overpotentials required for both the oxygen evolution reaction and the air-captured CO₂ reduction reaction need to be addressed.¹⁷⁴ Regarding the latter, electrolyte engineering with different carbon capture solutions could establish a balance between capture and conversion, facilitating rapid direct air CO₂ capture and its subsequent reduction at low potentials.¹¹² Replacing water oxidation with a more energetically favorable waste-derived substrate oxidation can also decrease the overall cell voltage requirement for air-captured CO₂ reduction (to ~1 V) while providing a way to valorize waste materials (Figure 8).¹⁷⁵

New earth-abundant metal-based electrocatalysts can be developed, moving away from noble metals (Au, Ag), which can retain activity in aerobic CO₂-capturing electrolytes.^{176,177} The long-term stability of captured CO₂ electrolyzers when operated at high current densities with high carbon conversion efficiencies remains to be explored. The use of bipolar membranes could be avoided when possible due to their high cost, relatively complex fabrication, and high transmembrane electrical resistance at high current densities.^{178,179} Additional operational complexities related to carbonate precipitation and CO₂ crossover across the membrane must be addressed before the systems can be scaled up. Furthermore, consideration should be given to optimizing the integration of photovoltaic modules with electrolyzers (either as separate units or integrated buried-junction units) to match the photovoltaic module's output voltage and current to the electrolyzer's load, to maximize solar-to-chemical efficiencies (Figure 8). Additional complexities arising from low CO₂ solubility in aqueous electrolyte solutions can be circumvented by moving to gas-phase systems.^{180–182}

Direct photochemical air-to-fuel conversion (Figure 6), powered by sunlight, can be developed in a straightforward, scalable setup with low capital expenditure, a key advantage of direct photocatalysis.^{183,184} However, the activities of direct photochemical systems remain too low for their commercial applications. The primary reasons for this are attributed to rapid charge-carrier recombination, incomplete light absorption, and degradation of photocatalyst activity over time.^{185,186} Recombination can be minimized by developing materials containing heterojunctions to ensure facile charge separation upon their photoinduced generation.^{187–189} Similarly, improved light absorption by developing visible-light-responsive photocatalysts needs to be pursued to utilize a broad solar spectrum.^{190,191}

During direct photocatalytic aerobic CO₂ reduction, care must be taken to separate fuels from air after photoconversion to avoid the dangers posed by air–fuel mixtures. Additional difficulty arises from the challenge of competing aerobic O₂ reduction. The dual-step approach introduced by us provides a workaround by concentrating CO₂ and removing O₂ in an upstream gas-phase process.⁷⁵ Still, the efficiencies in both solar CO₂ concentration and CO₂ conversion require improvement. The field will benefit from breakthroughs in photocatalyst development,¹⁹² leading to enhanced light absorption, charge separation, electron transfer, and stability, ultimately bringing it

closer to the desirable 5% solar-to-chemical efficiency target (Figure 8).^{131,193,194}

The Bionic Leaf technology employs a hybrid approach by utilizing natural systems to facilitate CO₂ fixation, which is often the most challenging aspect for aerobic CO₂ conversion, while generating the necessary energy through solar H₂ production (Figure 7). The bacteria can be genetically engineered to produce a variety of fuels and chemicals, providing access to products that are not readily accessible from purely synthetic devices.^{195,196} Further work can thus engineer bacterial strains for the synthesis of fine chemicals. The use of living organisms, however, requires that contaminants and the medium temperature be controlled during operation to prevent cell death.

Among future explorations, the scalability of this technology for carbonaceous fuel production can be investigated. The current major efficiency loss stems from the efficiency cap of the solar cell. The voltage and current matching between the photovoltaic output and the biohybrid electrolyzer input needs to be tuned to ensure the entire process operates at the maximum possible solar conversion efficiency.¹⁵⁴ As it currently uses a bacterial batch process for CO₂ conversion, the reaction rates should be optimized to achieve the highest possible CO₂ conversion from aerobic CO₂ in the shortest possible time. Overall, this technological approach holds promise but requires further development beyond its current stage, particularly in terms of scalability and economic viability (Figure 8).

5. OUTLOOK

Despite several advances, solar air-to-fuel technologies require substantial further development. The thermochemical route, though the most mature and capable of producing tangible air-to-fuel products, remains capital-intensive and operates at extremely high temperatures that challenge material and system stability. Moving toward lower reaction temperatures using alternative oxygen-transport materials will be crucial. Meanwhile, electrochemical systems, particularly direct carbonate, bicarbonate, and carbamate electrolyzers, show promise but require further research to improve carbon conversion efficiency, prevent crossover and precipitation, enhance stability, optimize energy use, and improve operational flexibility. Technoeconomic analyses under relevant industrial conditions are necessary, with a recent study identifying iridium costs from anodic water oxidation as a significant cost contributor in direct carbonate electrolysis for ethylene production.¹⁹⁷ Compared to the electrocatalytic air-to-fuel systems, current photocatalytic systems are at a lower TRL (2–3) due to their lower activity. Fundamental research in photocatalyst development for both gaseous and chemically captured CO₂ photoreduction is required to enhance catalytic efficiencies. Likewise, the biohybrid approach requires further study, particularly regarding system stability, long-term energy efficiency, and technoeconomic factors, before large-scale implementation can be considered.

The world consumes around 15 billion liters of crude oil per day, and substituting this vast amount with sustainable synthetic fuels from air is a massive challenge. Electrification and the hydrogen economy can make significant strides in decarbonizing some industrial sectors, including light transport, but synthetic fuels will be needed to meet the liquid fuel demands of the aviation, heavy transport, and chemical industries to produce plastics as well as bulk and fine chemicals with low carbon or net-zero emissions. The scientific community's interest in tackling this formidable challenge and making solar air-to-fuel a reality

has been evident over the past decade, with new partnerships, consortia, and research centers emerging rapidly.¹⁹⁸ However, major hurdles in the industrial and political spheres need to be overcome to realize this ambition and to implement commercial clean technologies. Support from government policies for the use of green synthetic fuels, even as a small fraction blended with current fuels, will be necessary for the early adoption of these emerging technologies and place them on the learning curve.¹⁹⁹ Harvesting and utilizing atmospheric CO₂ to store solar energy as fuels would enable us to effectively regulate atmospheric CO₂ levels and meet the energy demands of our civilization while enabling the adoption of a circular carbon economy.²⁰⁰ How effectively we can achieve this and how long it will take will have a decisive impact on our society's future.

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Notes

The authors declare the following competing financial interest(s): A patent application covering integrated direct air capture and utilization into solar fuels has been filed by the University of Cambridge technology transfer office, Cambridge Enterprise with S.K. and E.R. as co-inventors (application no GB2408950.0).

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