



# Perspective Unconventional and Emerging Approaches to CO<sub>2</sub> Reduction

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**Abstract:** This perspective highlights unconventional and emerging approaches to  $CO_2$  reduction. These methods encompass the use of topological materials and 3D printing in electrochemistry and the broader fields of plasma- and magneto-electrochemistry. Sustainability in these methods offers a way to convert  $CO_2$  into value-added fuels in a circular energy economy. We identify challenges of reducing  $CO_2$  along sustainable pathways and detail ways that unconventional approaches can address these challenges. These include achieving high product selectivity toward desirable chemicals, high catalytic durability, high energy efficiency, and high conversion rates of  $CO_2$ . Finally, we describe emerging impacts and opportunities of these unconventional approaches and key challenges.

**Keywords:** CO<sub>2</sub> reduction; electrochemistry; 3D printing; additive manufacturing; topological materials; plasma-electrochemistry; magneto-electrochemistry

# 1. Introduction

The demand for energy on a global scale has grown rapidly over the past half century and led to an ever-increasing consumption of fossil fuels. As a result, an astounding amount of carbon dioxide  $(CO_2)$  has been emitted into the atmosphere, reaching 37.5 billion tons in 2021 [1]. Unfortunately, unlike some greenhouse gases,  $CO_2$  remains in the atmosphere for lengthy periods of time (upwards of 200 years), which imparts sustained contributions to global warming and other environmental issues, such as flooding and sea-level rise [2]. In 2016, 195 parties signed the Paris Climate Accords as a pact to work actively towards the mitigation of climate change on a global scale [3]. Unfortunately, barring drastic and proactive measures, it is predicted that, at the current rate of  $CO_2$  emissions, the Earth will be 1.5 °C warmer than pre-industrial temperatures in as little as nine years [1]. Environmental agencies in the United States, such as the Environmental Protection Agency (EPA), have begun to impose regulations on  $CO_2$  emissions in attempts to curb such deleterious outcomes. Playing a significant role in the reduction of  $CO_2$  emissions is carbon capture and storage (CCS) [4–6]. The three most commonly used CCS techniques are post, pre, and oxy combustion, and although CCS technologies are being implemented, logistical and economic hurdles inhibit widespread utilization [7].

The reduction of  $CO_2$  is one method that is being used to sequester  $CO_2$  from the atmosphere and transform it into value-added chemicals. In these processes,  $CO_2$  is converted into useful fuels or commodity chemicals (e.g., carbon monoxide (CO), ethanol, formic acid, methanol, acetic acid, and others) using electrochemical, photochemical, or thermochemical processes (Figure 1) [8–14]. Detailed economic analysis of these approaches have been the subject of much research and investigation [15,16]. These processes integrate catalysts and supply external energy (i.e., electrical, process heating, etc.) to reduce activation barriers and drive the conversion of  $CO_2$ . However, when this energy comes from carbon-intensive processes, like the burning of hydrocarbon fuels,  $CO_2$  emissions can increase, especially along inefficient conversion pathways. Instead, pathways to reduce  $CO_2$  emission using reduction processes require the use of sustainable forms of energy. These pathways form a



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circular energy economy where the burning of fuels, production of  $CO_2$ , and conversion of  $CO_2$  balance to yield net-zero  $CO_2$  emissions [17].

**Figure 1.** Sustainable  $CO_2$  reduction is a pathway to limit  $CO_2$  emissions and form value-added chemicals in a circular energy economy. (**A**) Conventional reduction methods include electrochemical, photochemical, and thermochemical approaches. (**B**) Emerging and unconventional methods include the use of topological materials, 3D printing and additive manufacturing, plasma electrochemistry, and magneto-electrochemistry. In the figure, X, Y,  $e^{-}_{(aq)}$ , and jxB refer to  $CO_2$  reduction products, co-reactants, solvated electrons, and the Lorentz force, respectively. T and P refer to the temperature and pressure at which thermochemical reduction of  $CO_2$  occurs.

Electrochemistry is one pathway to CO<sub>2</sub> reduction (CO<sub>2</sub>R) that can integrate sustainable forms of electrical energy. In these processes, electrocatalysts have proven useful in reducing  $CO_2$  to various benign and useful products [18]. However, as with all sustainable pathways, the scalability of these processes is limited by their capacity to maintain high product selectivity, long-lasting catalytic stability, energy efficient conversion, and rapid reaction rates. Innovation continues within electrochemistry to identify new electrocatalysts that promote CO<sub>2</sub> reduction, limit unwanted competing reactions, and remain economically viable (i.e., using abundant materials). For example, to maintain high energy densities using electrocatalysts, reactions that compete with CO<sub>2</sub>R, such as hydrogen evolution (HER), must be minimized. This has been achieved by incorporating materials into catalysts that have minimal activity toward the reduction of hydrogen [19–21]. Many catalysts are also prone to oxidation, which can lead to problems in solutions that have drastically higher concentrations of O<sub>2</sub> compared to atmospheric levels. While expensive and sparsely abundant noble metal electrocatalysts (e.g., Au, Ag, Pt, Pd, Ir, Ru) have exhibited many of these performance metrics, wide-spread use is hampered by their high cost. Alternatively, researchers have investigated a host of other materials as candidate electrocatalysts including metal-organic frameworks (MOFs), layered double hydroxides, transition metal-oxides/sulfides/nitrides, and single atoms (often supported on graphene) [22–27]. Gaining momentum in the construction of low-cost, highly active electrocatalysts is the incorporation of earth-abundant materials (e.g., Co, Sn, Cu, Ni, Si). For example, owing to its chemical stability, earth-abundance, high conductivity, and access to multiple oxidation states, cobalt-based electrocatalysts have proven to be exceptionally well-suited for CO<sub>2</sub>R, demonstrating high catalytic performance [28–30]. Interestingly, catalysts consisting of the earth-abundant metal copper (in its pure form) have been shown to generate as many 14 different highly reduced products in aqueous neutral pH conditions [31,32]. Copper catalysts are also the only pure metal capable of forming the more complex multi-carbon ( $C_2$ 

or greater) reduction products. However, one drawback is the high overpotentials required to reach even moderate electrochemical activities. To address these issues, researchers have begun to look for alternatives to Cu that may lead to enhanced selectivity in product formation as well as more reasonable overpotentials. Ni-based catalysts have emerged as a potential candidate because Ni is the only other pure metal that has been reported to reduce  $CO_2$  to highly reduced products [31].

The widespread integration of sustainable  $CO_2R$  requires processes to achieve scalable and efficient utilization of  $CO_2$  into value-added chemicals. Electrochemical pathways, in particular, require innovations to rethink the type of electrocatalyst, its fabrication process, and the details of electrochemical reaction environments through which reactions proceed. These improvements could rethink the thermodynamics of electrochemical reactions by introducing solvated electrons, incorporating magnetic fields to induce bulk convection, or incorporating new classes of materials with higher and more selective catalytic activity. This perspective will outline emerging approaches that can address these needs by integrating topological materials, 3D printing, plasma-electrochemistry, and magneto-electrochemistry to  $CO_2R$  (Figure 1B). Details will be given about how these approaches address challenges with scaling  $CO_2R$  to enable a circular energy economy.

#### 2. Emerging Approaches

Electrochemical and sustainable CO<sub>2</sub>R uses electrical energy to drive chemical reactions at an electrocatalyst. The feasibility of these processes depend on the efficiency by which electrical energy can be used to convert CO<sub>2</sub>, how long reactions can proceed (i.e., durability of catalysts), how selectively value-added products can be produced, and the overall cost to operate a reactor. Emerging approaches to  $CO_2R$  target the type and properties (e.g., durability, etc.) of electrocatalysts along with the details of the environment in which they are placed. For example, solutions at the intersection of chemistry, material science, and physics are rethinking the ingredients of electrochemical reactions and reimagining how catalysts can synergize with the environment that surrounds them. By leveraging this intersection, the design space of electrochemical systems can broaden beyond just considering the properties of materials, bulk transport of reactants, or the thermodynamic environment in which reactions proceed and instead consider how they can be designed together. Interdisciplinary areas for electrochemical CO<sub>2</sub> reduction, including topological materials, plasma-electrochemistry, magneto-electrochemistry, and 3D printing, are all promising research areas with the potential to impact challenges that limit the performance and scalability of electrochemical processes (Table 1).

**Table 1.** Emerging approaches to CO<sub>2</sub> reduction can help address performance challenges and scalability constraints of more conventional electrochemical processes.

Challenge	Positive Influence of Emerging Approaches			
	<b>Topological Materials</b>	Magneto-Electrochemistry	Plasma-Electrochemistry	3D Printing
Product Selectivity	,			,
Catalyst Durability	$\checkmark$			$\checkmark$
Faradaic Efficiency	$\checkmark$	$\checkmark$	$\checkmark$	
Reaction Rate	$\checkmark$	$\checkmark$	$\checkmark$	

## 2.1. Topological Materials

Very recently, researchers interested in energy storage and conversion applications have begun to investigate the use of Topological Materials (TMs) [33–37]. TMs can be loosely divided into two classes: Topological Insulators (TIs) and Topological Semimetals. Topological Semimetals include Dirac Semimetals (DSMs), Nodal-Line semimetals (NLS), and Weyl semimetals (WSMs). Topological semimetals can be characterized by their surface states (which are induced by the topology of their bulk band structure) [38]. Like Dirac fermions found in graphene, Weyl fermions are robust electrons that have substantial

mobility and only depend on translation symmetry [39]. It has been proposed that the surface of WSMs contain Fermi arc electron states, which are projected from Weyl nodes residing in the bulk crystal [40]. An inversion of the valence and conduction bands (through spin-orbit coupling) generates their topological surface states. Recently, TMs have been investigated experimentally for their catalytic ability, although much of the focus has been on the hydrogen evolution reaction (HER) [41]. Here, researchers have uncovered interesting properties such as high durability (over 12 h) and remarkably high activity. Curiously, size-dependent catalytic activity of WSMs has been reported, which is opposite to the behavior observed with noble-metal based electrocatalysts where nanomaterial results in higher activity based on surface area; WSMs show negligible activity at this length-scale [42].

To date, there are few examples of TMs being tested experimentally as electrocatalysts for the  $CO_2$  reduction reaction, however, the results have been extremely promising. Huan Xie et al. used single-crystalline Bismuth rhombic dodecahedrons (Bi-RD) (with (104) and (110) exposed facets), a topological insulator, towards  $CO_2R$  [43]. Interestingly, they found that the Bi-RD TI resulted in a low overpotential of 120 mV and high selectivity towards formate with a faradaic efficiency of ~92%. Moreover, the high selectivity for formate production was observed over a wide current density range (between 9.8 and 290.1 mA cm<sup>-2</sup>); this contrasts with most reported Bi-based electrocatalysts, which are only selective for formate generation over narrow potential windows. The increased selectivity and low overpotentials were ascribed to the preferential and enhanced adsorption of \*OCHO on the Bi-RD surface. Xijun Liu et al. demonstrated the utility of ultrathin MoTe<sub>2</sub> layers, belonging to the WSM class of TMs, towards the electrocatalytic reduction of  $CO_2$  to  $CH_4$  [44]. To circumvent known  $CO_2$  solubility issues in aqueous media, they used an ionic liquid as the electrolyte (1-butyl-3-methylimidazolium tetrafluoroborate). Although at low potentials  $CO_{(g)}$  and  $H_{2(g)}$  were the dominant products, at -1.0 VRHE, the electroreduction of CO<sub>2</sub> to methane reached a maximum faradaic efficiency of 83%. Impressively, the MoTe<sub>2</sub> WSM displayed a durability of 45 h at 25 mA cm<sup>-2</sup>. Other researchers have taken a computational approach towards investigating the utility of TMs towards  $CO_2R$ . For example, Mengyu Tang et al. showed that the Topological NLS,  $Cu_2Si$ , has a strong reduction ability to activate  $CO_2$  to \*COOH in the selective formation of CH<sub>4</sub> [45]. Such computational studies are an important contribution to the growing field of TM electrocatalysts and will only serve to inspire other researchers to interrogate them experimentally.

#### 2.2. Plasma-Electrochemistry

The intersection of low-temperature plasma (i.e., electron temperature >> gas temperature) and electrochemical processes is an emerging path to reduce  $CO_2$  using electrical energy. The addition of plasma, or ionized gas, extends the conductivity of electrochemical cells to the gaseous phase (e.g., Ar, He, etc.) by imposing higher field strengths (~kV) to break down gases, form free electrons, and sustain discharges. This is distinct from electrochemical reduction reactions where electron transfer is confined to surfaces sites where reactant molecules are adsorbed. Unlike these reactions, plasmas (1) generate free electrons in a volume and (2) can tune the mean kinetic energy of electrons by adjusting the strength of an imposed electric field. This rethinks where and how electron transfer happens in electrochemical reactions and eliminates the need for reactants to adsorb first onto electrocatalysts [46]. When plasmas are added, free electrons can drive electrochemical reduction reactions by terminating on gas-liquid interfaces. This introduces solvated electrons at interfaces that penetrate into the volume of an electrolyte, drive chemical reactions, and eliminate constraints on the surface area of electrocatalysts and the diffusion layers that form near them. Moreover, the tunability of the electron energy in plasma processes enables a level of control over product selectivity that is independent of the properties of an electrocatalyst. This control has been shown to target rate-limiting steps, break scaling constraints, and enable the design of completely new catalysts in heterogeneous catalytic

systems [47]. Extending these ideas to electrochemical reactions is one way to broaden the design space of electrocatalysts and improve the performance of CO<sub>2</sub>R.

Plasma-electrochemical systems use interfacial fluxes of free electrons (i.e., from gaseous molecules) and UV photons (i.e., radiolysis produced from bound-bound and free-free emission in the plasma) to drive the reduction of CO<sub>2</sub>. Much like radiolysis, where UV photons from light sources can liberate solvated electrons in solutions, fluxes of free electrons from plasmas can penetrate into liquids that are saturated with CO<sub>2</sub> and drive chemical reactions. For example, once electrons are solvated, CO<sub>2</sub> that is in the liquid phase (CO<sub>2(aq)</sub>) can be reduced,  $e^{-}_{(aq)}$  by  $e^{-}_{(aq)} + CO_{2(aq)} \rightarrow CO_{2^{-}(aq)}$ , to form a carboxyl radical anion (CO<sub>2<sup>-</sup>(aq)</sub>) [48]. The carboxyl anion is a reactive intermediate that can then form a variety of products, including both oxalate (CO<sub>2<sup>-</sup>(aq)</sub>)<sub>2</sub> and formate (HCO<sub>2<sup>-</sup>(aq)</sub>). To form oxalate, CO<sub>2<sup>-</sup>(aq)</sub> can undergo a recombination reaction [49]. In acidic conditions, carboxyl ions form HCO<sub>2<sup>-</sup></sub> through equilibrium reactions with H<sup>+</sup> [50]. Solvated electrons can also reduce water to form H<sub>2</sub> and hydroxide (OH<sup>-</sup><sub>(aq)</sub>), 2e<sup>-</sup><sub>(aq)</sub> + 2H<sub>2</sub>O  $\rightarrow$  H<sub>2</sub> + 2OH<sup>-</sup><sub>(aq)</sub>.

To date, experimental studies of plasma-electrochemical reduction of CO<sub>2</sub> have suffered from low faradaic efficiencies and high energy costs. Work has shown total faradaic efficiencies toward both oxalate and formate up to ~8.9%, with current densities up to ~795 mA/cm<sup>2</sup> [46]. Higher faradaic efficiencies toward CO<sub>2</sub> reduction are limited by the amount of CO<sub>2</sub> that can be dissolved in water and competing hydrogen production. Challenges aside, computational studies have shown how pulsed discharges (i.e., only applying the plasma for ~0.04 s) and transport effects can increase the faradaic efficiency of plasma-electrochemical processes dramatically. By using nanoliter flow reactors with pulsed discharges, the faradaic efficiency of CO<sub>2</sub>R was shown to increase to ~98%, with 97% product selectivity toward oxalate [51].

## 2.3. Magneto-Electrochemistry

The use of magnetic fields is one approach to increase the reaction and scalability of electrochemical  $CO_2R$ . Examples of using magnetism in electrochemistry can be broadly categorized into four effects: (1) magnetohydrodynamics (i.e., magnetic fields inducing bulk convection in an electrolyte), (2) chirality-induced spin selectivity (i.e., using magnetic electrodes to inject electrons with known spin), (3) magnetophoresis (i.e., using magnetic fields to control paramagnetic species), and (4) stabilization of radical pairs [52–55]. While each of these effects have shown some potential to increase the yield or reaction rate of electrochemical processes, mechanistic insight is still missing.

Magnetohydrodynamics, in particular, has been shown to influence the performance of CO<sub>2</sub>R. In this regime, magnetic fields are known to interact with the flow of current in electrochemical cells to drive bulk convection, compress diffusion layers, and drive products off of electrocatalytic surfaces [56]. These performance benefits are achievable without moving the electrodes or the electrochemical cell, and instead are possible by simply placing a permanent magnet (or electromagnet) close to an electrocatalyst where current is flowing. When an imposed magnetic field is perpendicular to the direction of current flow, a Lorentz force is applied to the electrolyte, jxB, in a plane perpendicular to the direction of current flow and the magnetic field. The Lorentz force contributes momentum to the electrolyte (i.e., induces a velocity) in the bulk and near electrocatalytic surfaces, where other magnetic field forces, including paramagnetic forces and  $\nabla B$  forces, contribute to ionic transport. When magnetohydrodynamic convection extends to the surface of electrocatalysts, the induced flow can drive bubbles off surfaces and limit the poisoning of catalytic surfaces with unwanted product accumulation. These magnetic field transport effects have also been observed to increase the diffusion-limited flow of ions by reducing the thickness of boundary and diffusion layers, increase the flow of current in amperometric conditions, and lower the overpotential of an electrochemical reactions, including the reduction of  $CO_2$ .

To date, experimental studies of magnetohydrodynamic transport in  $CO_2R$  have demonstrated a 130% increase in operating current density when a 0.3 T magnet was placed

adjacent to an electrochemical cell [54]. These experiments used a polycrystalline Cu foil as a cathode, Pt wire as an anode, and an aqueous solution of  $1 \text{ M KHCO}_3$  (which served as a buffer, source of  $CO_2$ , and an electrolyte). Separate experiments flowed  $CO_2$  through a gas diffusion electrode. Experimental trends were measured to scale  $(j/j_0)$ , where  $j_0$  is the current density before a magnet is applied) with the magnetic field strength (*B*) as  $\propto B^{0.08}$ . This scaling is lower than theoretical predictions  $(B^{2/3})$  and was attributed to the generation of bubbles on electrocatalysts that influence the mass transport of reactants. However, it was also found that by increasing the surface area of the electrodes, current density of the cell, or viscosity of the solvent, a non-monotonic increase in  $j/j_0$  could be produced when a magnetic field was applied. Magnetohydrodynamic effects have also been shown to influence the product selectivity of  $CO_2R$  relative to HER. Measurements showed that the application of a magnetic field increased the amount of  $CO_2R$  products (i.e., CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, etc.) relative to H<sub>2</sub> gas across potentials ranging from 0.7–1.1 V versus a reversible hydrogen electrode (RHE). The selectivity of CO<sub>2</sub>R products were measured and were showed to increase by 250% compared to conditions when no convection was present at 0.95 V versus RHE and 150% compared to conditions when the cell was mechanically mixed with a motor at 1.1 V versus RHE [57].

# 2.4. 3D Printing

As a technology, additive manufacturing (i.e., 3D printing) is playing an ever-increasing role in scientific endeavors, ranging from analytical chemistry to energy storage [58–66]. The ability to rapidly print various prototypes and test them has resulted in 3D printing becoming a fixture in many research laboratories. While there are many different forms of 3D printing, arguably the two most utilized are (i) Stereolithographic (SLA) and (ii) Fused-Deposition Modeling (FDM).

SLA 3D printers use a UV light source (i.e., UV laser) to polymerize a photocurable resin. These SLA 3D printers are commonly in one of two configurations: (i) free platform configuration and (ii) inverted geometry (top-down configuration) [67-69]. Using the free platform configuration, the print bed (i.e., build platform) begins at the top of a reservoir tank containing the photocurable resin and moves towards the bottom of the reservoir tank after each layer of the desired structure is printed, finishing when the predetermined number of layers have been printed. In the top-down configuration, the print bed begins at the bottom of the reservoir tank and the photocurable resin is cured as the platform is raised. The resin is polymerized, via a movable laser (or one that is fixed with accompanying mirrors) at the build platform, into a solid structure where each twodimensional layer solidifies and melds with the previously cured layer. Not surprisingly, variations of SLA printings have also been reported, such as two-photon polymerization (2PP). 2PP relies on a modification of the laser optics and is capable of improving feature resolution down to the nanometer length scale [70]. Of all the 3D printing techniques currently available, 2PP has superior resolution and is capable of fabricating high-quality optical surfaces and microstructures with considerable complexity. Unfortunately, the high cost and advanced technical skills required to operate 2PP prohibit its broad use. Digital light processing stereolithography (SLA-DLP) is another modification of the SLA type 3D printer. One benefit of SLA-DLP is the superior print speed, which is achieved using a digital micromirror as the projector that simultaneously impinges upon and polymerizes the entire build surface as opposed to rastering with a single source [71].

FDM is one of the major commercial versions of 3D printing, owing to its cost and simplicity of use; it extrudes material (e.g., filament) to create structures based off predetermined designs [72]. FDM can print diverse materials such as acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), polystyrene, polycarbonates, polyethylene terephthalate (PET), polyvinyl alcohol (PVA), polyamide (i.e., Nylon), polycaprolactone (PCL), polybutylene terephthalate (PBT), and polyglycolic acid (PGA) [73,74]. Interestingly, carbon-based conductive thermoplastics have also become commercially available, providing unique opportunities for fabricating carbon-based materials for diverse applications such as sensing and catalysis. The fabrication process involves heating a filament beyond its glass transition temperature and extruding it through a heated nozzle. The material quickly cools once extruded and solidifies and each subsequent layer fuses to the preceding layer as it cools. Unfortunately, structures created using FDM can be considerably less robust than those fabricated using SLA due to the lack of chemical fusing [75]. Additionally, when compared to other 3D printing techniques currently available, FDM printing has the lowest resolution. The resolution of FDM printing is highly printer dependent, and the extruder nozzle is the primary mechanism for adjusting the resolution (typically on the order of 500  $\mu$ m) [76].

Coupling the cost effectiveness of 3D printing with the increasing material compatibility of various 3D printing technologies, researchers have begun to explore the utility of 3D printing in the realm of electrocatalysis. In comparison to traditional manufacturing techniques such as drilling or milling, 3D printing relies on a layer-by-layer process to fabricate materials with defined structures and geometries (also permitting the creation of internal structures) [77]. This approach inherently leads to less waste material, leading many to consider 3D printing as a promising "green" technology in the manufacturing landscape. Electrolyzers, whether for the  $CO_2$  reduction reaction ( $CO_2RR$ ) or water splitting, are composed of both conductive (i.e., electrodes/catalysts) components and non-conductive (i.e., reactors/cells) components. Owing to the technological advancements in 3D printing machines, particularly the development of dual/triple extruder nozzles, both conductive and insulator materials can be printed simultaneously. This permits the fabrication of housings, conductive electro-active materials, and flow-fields (for electrolyte/gas transportation) to be integrated with novel design strategies. Although traditional manufacturing approaches allow for the subsequent assembly of machined parts into a single device, this approach does incur additional time and introduces the possibility of human error. It should be noted that, owing to its status as an emerging technology, most applications of SLA and FDM 3D printing towards electrochemical CO<sub>2</sub> reduction are focused on cell/reactor design, and we guide the reader to a more in-depth commentary solely focused on 3D printing in CO<sub>2</sub> reduction [78].

A hurdle in the seamless application of 3D printed conductive material is that commercially available filaments are largely composed of non-conductive thermoplastics such as PLA or ABS. Upon printing, researchers have found that these carbon-infused thermoplastics have minimal electroactivity and require post-processing steps to improve electrochemical behavior [79]. Various activation protocols have been proposed (e.g., saponification in strongly alkaline media, soaking in organic solvent, electrochemical, etc.) with the aim of stripping away the non-conductive material from the electrode surface, thereby exposing the active carbon material [80–82]. Furthermore, electrocatalysts are often comprised of metallic nanomaterial, which requires additional post-processing to endow 3D printed material with their catalytic properties. Impressively, although this does add an additional time element in the "print-to-use" workflow, 3D printed materials are finding extreme utility in the electrocatalytic  $CO_2$  reduction reaction. The first example of applying 3D printing towards the fabrication of catalysts towards the electrochemical reduction of CO2 was introduced by Eva Vaneckova et al. in 2021 [83]. Using a commercially available filament composed of PLA and carbon nanotubes (PLA-CNT), they used FDM printing to fabricate square electrode surfaces with a geometrical area of  $6.4 \times 10^{-5}$  m<sup>2</sup>. The asprinted electrodes were then functionalized through Cu electroplating. The resulting Cu-modified 3D printed PLA-CNT catalyst demonstrated a maximum faradaic efficiency (FE) of 39% towards the production of formate from a CO<sub>2</sub> saturated solution (containing  $0.5 \text{ M KHCO}_3$  as the supporting electrolyte). These results are well aligned with FE's reported in the literature for other Cu-based electrocatalysts. Importantly, this demonstrates the utility of FDM-based 3D printing towards future developments in combating CO<sub>2</sub> emissions.

#### 3. Technical Challenges and Outlook

In this perspective, we highlighted four emerging research areas that we believe will contribute significantly to future advancements in electrochemical  $CO_2$  reduction. Individually, TMs, magneto-electrochemistry, plasma-electrochemistry, and 3D printing have made contributions towards making  $CO_2$  reduction a scalable and sustainable process. For example, the high activity of TMs towards water-splitting, magnetohydrodynamic transport effects in batteries and supercapacitors, synergistic catalytic design in plasma processes, and the rapid manufacturing of low-cost analytical tools using 3D printing are just a few of their impressive applications. While the benefits of such approaches appear clear and warrant a concerted research effort towards obtaining deeper understanding of their influence with more experimental validation, each research area is still in its infancy with respect to the  $CO_2$ RR. Below we highlight some of the important unknowns and research opportunities related to these emerging approaches (Table 2).

Table 2. Open questions in promising areas of research for CO<sub>2</sub> reduction.

Research Area	Open Questions	
Topological Materials (TMs)	Do topological surface states influence product selectivity?	
	What is the importance of surface-based active sites?	
	What causes the enhanced durability of TMs?	
Plasma-Electrochemistry	How can the energy cost of plasmas be reduced?	
	How can electron energy distributions be controlled?	
	How do plasma excitations change reaction pathways?	
	What is the role of solvated electrons?	
	What synergies exist with electrocatalysts?	
Magneto-Electrochemistry	How do MHD effects change reaction rates?	
	How do magnetic fields change reaction pathways?	
	How do magnetic fields change product selectivity?	
	What synergies exist between electrocatalysts and magnetic fields?	
	Does geometrical control over catalyst dimensions change product selectivity?	
3D Printing	Will unique catalyst design result in more durable catalysts?	
Ū.	What role do impurities have in overall catalyst performance?	

# 3.1. Topological Materials

While the investigation and incorporation of TMs has been increasing recently, the exact mechanisms behind their surprisingly high catalytic activity and durability require more investigation. Electrocatalytic processes occur at the surface of the catalysts; hence, the electronic structure and geometry of the surface atoms are critical in the optimization of electrocatalytically active materials. TSSs seem to be robust towards  $CO_2$  reduction, where robustness of the TSS originates from the bulk band structure (when the bulk band structure is intact, the TSS remains active). Large anomalous Hall conductivity has also been discovered in these materials, which has yet to be sufficiently explored in electrocatalysis [84]. Furthermore, there are only a handful of reports on TM-based electrocatalysts being employed in nonaqueous electrolytes; this is important since the poor solubility of CO<sub>2</sub> in aqueous media (~35 mM) can be overcome using ionic liquid or organic electrolytes. Importantly, the choice of electrolyte has been shown to be an important factor in product formation [85]. In fact, even in aqueous systems, the solution composition (pH, identity of cations and anions) has been shown to strongly influence selectivity [86]. Lastly, thanks to the efforts of many researchers, there exists an easily accessible database for identification of TMs [87]. In the coming years, more researchers will employ these interesting materials, take advantage of their unique properties, and validate the use of many different TMs towards the  $CO_2RR$ .

#### 3.2. Plasma-Electrochemistry

The integration of plasmas in electrochemical environments is an emerging approach to increase reaction rates, eliminate adsorption steps, and increase the scalability of electrochemical reactions toward high current densities. However, the broader integration of plasmas in CO<sub>2</sub>R depends on their ability to reduce CO<sub>2</sub> to desirable products selectively while limiting the energy costs of sustaining a plasma discharge. Mechanistic studies to optimize the flux of free electrons and UV photons from plasmas, their energy, and application timescale while also uncovering synergistic roles with electrocatalysts are all fundamental questions that remain to be explored. The intersection of design between electrocatalysts and plasmas, along with the minimization of energy costs to sustain plasmas in the gas phase, will be key to achieving feasible  $CO_2R$  with plasma-based technologies. Without these advances, the reactivity of solvated electrons will constrain the performance of the processes. While these electrons can eliminate the need for reactant adsorption, they create basic conditions locally at interfaces, form OH<sup>-</sup>, and generate reactive intermediates that undergo branching reactions that limit the generation of desirable products like CH<sub>3</sub>OH, CHO, and HCOOH. Moreover, their concentration at gas-liquid interfaces, and thus feasibility at large scales, is constrained by the flow of current and conductivity of solutions (~1 mM in most conditions). Opportunities exist to design the gas-liquid interface in plasma-electrochemical environments, including adding catalysts to leverage the reactive flux of electrons and UV photons and drive the production of desirable CO<sub>2</sub>R products.

# 3.3. Magneto-Electrochemistry

Magnetic fields can change the selectivity and reaction rates of electrochemical processes. They can be integrated by simply placing a magnet (i.e., permanent or electro-) close to a catalytic surface where current is flowing. While their integration is comparatively simple compared to other unconventional approaches, mechanistic insight into how they should be integrated and which effect (i.e., magnetohydrodynamics, chirality-induced spin selectivity, magnetophoresis, and stabilization of radical pairs) they should drive remains. Of these, magnetohydrodynamics, in particular, has been shown to influence the electrochemical reduction of  $CO_2$ . However, mechanistic descriptions of how Lorentz forces evolve, generate convection locally in diffusion layers, and drive the convection of bubbles off of electrode surfaces (i.e., liquid-bubble interface) is needed. Furthermore, approaches are needed to integrate Lorentz forces and magnetic fields to induce mixing locally and eliminate concentration polarization effects near GDEs in electrolyzers. Collective insights about how magnetic-induced transport couples to electrochemical reactions and how this transport can be designed locally in electrochemical cells have the potential to increase the performance of  $CO_2R$  across a broad range of conditions.

# 3.4. 3D Printing

The use of 3D printing in the development of efficient  $CO_2R$  electrocatalysts is likely to see a surge in interest in the coming years. In collaboration with engineers and materials chemists, new functional materials will be printed with tailorable performance and selectivity. Unfortunately, these materials advancements will likely not be commercial products for some time. In the meantime, and towards taking advantage of the unique benefits of 3D printing, researchers can use filament extruder and hopper instruments to develop "in-house" functional filaments. This approach has the advantage of controlling the composition (and in turn the properties) of the material to be printed and may lead to materials that are "ready-to-use" towards the electrocatalytic reduction of  $CO_2$ . The ability to incorporate highly active nanomaterials, 2D-layered material, polymers, etc., may alleviate the need for any post-processing procedures. 3D printing could also be used to fabricate specific catalyst geometries that permit the inclusion of low-cost, low-profile magnets seamlessly in order to take advantage of localized magnetic fields on a catalyst surface.

# 4. Conclusions

This perspective centers on four emerging and unconventional approaches aimed at addressing one of society's most pressing issues: CO<sub>2</sub> conversion. Abundant scientific evidence has documented and predicted the consequences of unchecked CO<sub>2</sub> emissions, resulting in enduring environmental effects such as global warming, damage to ecosystems, and rising sea levels, among others. To combat the deleterious impacts of  $CO_2$ on the environment, new approaches which take advantage of (i) emerging technologies (i.e., 3D printing), (ii) novel materials (i.e., topological materials), (iii) well-known but often ignored forces (i.e., Lorentz force), and (iv) efficient and synergistic processes (i.e., plasma-electrochemistry) should be utilized and exploited. These approaches offer potential beneficial influences on some of the most important experimental performance metrics such as: (i) product selectivity, (ii) catalyst durability, (iii) faradaic efficiency, and (iv) reaction rate. In terms of scalability and potential for industrialization, plasma-electrochemistry and 3D printing hold great promise. Plasmas have already found utilization in various industrial applications ranging from the microelectronics industry to the surface treatment industry. 3D printing, while still a relatively young fabrication method, has the ability to rapidly mass produce catalytic surfaces, or surfaces onto which catalyst can be loaded. The use of relatively large permanent magnets represents a potential roadblock to industrial-relevant scaling, although electromagnets may offer an alternative to the use of strong rare-earth magnets. While topological materials have the potential to reach industrially relevant durability and faradaic efficiency benchmarks, the synthesis of these materials can be time-consuming and cost intensive. In the realization of meaningful advancements in these emerging areas, the importance of interdisciplinary collaborations cannot be overstated. Materials chemists, engineers, and physicists will play crucial roles, not only in creating new catalytic materials but also in seamlessly incorporating them into devices. This integration is essential for leveraging factors such as local magnetic fields or plasma processes to enhance the performance metrics of the  $CO_2RR$ . Although the influence of these methods on the development of the next generation of electrochemical  $CO_2$  conversion processes is uncertain, focused research in these domains is bound to generate new scientific ideas and foundational research questions. It will also provide valuable insights into optimizing the utilization of these technologies, materials, forces, and processes to advance sustainability-related outcomes.

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