Upcycling air pollutants to fuels and chemicals *via* electrochemical reduction technology

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Abstract:

The intensification of fossil fuel usage results in significant air pollution levels. Efforts have been put into developing efficient technologies capable of converting air pollution into valuable products, including fuels and valuable chemicals (e.g., CO_2 to hydrocarbon and syngas and NO_x to ammonia). Among the strategic efforts to mitigate the excessive concentration of CO_2 and NO_x pollutants in the atmosphere, the electrochemical reduction technology of CO_2 (CO_2RR) and NO_x (NO_xRR) emerges as one of the most promising approaches. It is even more attractive if CO_2RR and NO_xRR are paired with renewables to store intermittent electricity in the form of chemical feedstocks. This review provides an overview of the electrochemical reduction process to convert CO_2 to C_1 and/or C_{2+} chemicals and NO_x to ammonia (NH_3) with a focus on electrocatalysts, electrolytes, electrolyzer, and catalytic reactor designs toward highly selective electrochemical conversion of the desired products. While the attempts in these aspects are enormous, economic consideration and environmental feasibility for actual implementation are not comprehensively provided. We discuss CO_2RR and NO_xRR from the life cycle and techno-economic analyses to perceive the feasibility of the current achievements. The remaining challenges associated with the industrial implementation of electrochemical CO_2 and NO_x reduction are additionally provided.

1. Introduction

Air pollution is one of the most significant challenges that humanity is currently facing. Massive utilization of non-renewable fossil fuels, various industrial and anthropogenic activities, power and electricity generations, engine combustions, and transportation have raised the level of pollution emitted into the atmosphere, which leads to more severely detrimental effects such as climate change, rain acidification, environmental degradation, and even the increasing health risk (Bai et al., 2022; Dominski et al., 2021; Kampa and Castanas, 2008; Markozannes et al., 2022; Saleem et al., 2022; Vallero, 2014). Nitrogen oxides (NO_x), carbon dioxide (CO_2), carbon monoxides (CO), and sulfur oxide (SO_x) account for ~85% of total air pollution (Asghar et al., 2021; Chen et al., 2020). Despite plenty of efforts to use more renewable and sustainable energy sources (Zhu et al., 2022), the fact that fossil fuels will at least remain a vital energy source for the next few decades making air pollution control difficult for the time being.

Developing sustainable processes by utilizing air pollutants directly as raw materials to produce chemicals *via* electrochemical conversion opens opportunities in different sectors, including valuable compound production from recycling waste in the industrial sector and chemical storage from intermittent renewable sources in the energy sector. To mitigate CO_2 pollution, it is technically accessible and energy efficient to reduce net CO_2 emissions by carbon capture, utilization, and storage (CCUS) technologies. The feasibility of CCUS to generate valuable products from polluting CO_2 adds economic and environmental benefits by eliminating the costs of storing CO_2 and lowering its leakage (Zhu et al., 2022). As for NO_x, a common term for nitrogen oxide species (e.g., NO, N_2O, N_2O_3, NO_2, N_2O_4, NO_3, and N_2O_5), technology has been developed to remove NO_x from the atmosphere in various ways, including advanced combustion to prevent NO_x formation and NO_x capture for the further conversion process. To date, selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) are the most popular industrial approaches to treating and converting NO_x into less harmful compounds. However, these processes have some drawbacks being prohibitive costs, ammonia slip, and the inability to produce N_2 with additional values.

Among the innovative attempts being investigated, the application of electrochemical CO_2 reduction reaction (CO_2RR) to value-added products (i.e., carbon monoxide (Ma et al., 2021; Shen et al., 2015; Zhong et al., 2020), formic acid (Agarwal et al., 2011; Ai et al., 2022; Aldaco et al.,

2019; Thonemann and Schulte, 2019), ethylene (Ai et al., 2022; Khoo et al., 2020; Ma et al., 2020), methanol (Guzmán et al., 2021; Irabien et al., 2018; Rumayor et al., 2019), ethanol (Guo et al., 2022; Karapinar et al., 2021; Xu et al., 2020), etc.) and electrochemical NO_x reduction reaction (NO_xRR) to ammonia (NH_3) (Daiyan et al., 2021; Hao et al., 2022; Ko et al., 2022; Soto-Hernández et al., 2019; Xue et al., 2021) is ones of which have the advantage of reducing the ever-growing CO_2 and NO_x pollutants and has received massive attention for the possibility of numerous commercial pathways. Converting waste (CO_2 and NO_x) back to raw materials is a promising route to minimize emissions and relieve the reliance on non-renewable resources for production while responding simultaneously to the need for chemical products. Using electricity from renewable sources such as solar or wind to drive the CO_2RR and NO_xRR paves the way for these emerging technologies to industrial practices. The intermittent renewable energy can be easily stored in chemical bonding (intermediate chemicals or fuels) for various applications. **Fig. 1** represents a schematic of the upcycling waste-to-chemical cycle. By offering numerous benefits of flexible reaction parameters, eco-friendly mechanisms, and convenience for large-scale implementation, the research community has thus appreciated electrochemical reduction technology. In addition, the electrolytes used in this technology can be recycled, reducing chemical consumption and simultaneously preventing waste liquid production. We have identified that electrochemically converting CO_2 and NO_x are highly efficient, scalable, flexible, and low in energy consumption and capital costs.

With the promising prospect, electrochemically converting CO_2 and NO_x pollutants into chemicals is, however, a challenging task. Since CO_2 is a thermodynamically stable molecule, it necessitates immense energy to break and activate of C=O bond. Moreover, the subsequent CO_2 reduction reactions are complicated as multiple elementary reactions, and proton-coupled electron transfer (PCET) are involved in generating diverse chemicals. Major CO_2RR occurs at an almost similar potential to the competing hydrogen evolution reaction (HER), making the selectivity of CO_2RR to a specific product relatively low (Seh et al., 2017). The NO_xRR is similar to CO_2RR, which involves multiple protons-electron coupling reactions and stable intermediates. The low solubility of some NO_x species (e.g., NO =1.94 mM at 25°C) in water will undeniably affect the conversion rate of NO_x in the electroreduction environment. As the benchmark, Cu-based CO_2RR and NO_xRR have low conversion efficiency, although their facile fabrication routes and abundance offer economic interests. Therefore, the development of CO_2RR and NO_xRR has focused more on

designing active catalysts and effective reaction conditions (e.g., electrolytes, electrolyzer, reactor cell design, etc.) to achieve high efficiency for each desirable chemical.

Numerous reviews discussed aspects of CO_2RR, from electrocatalysts searching and novel discoveries (by a well-designed experiment or high-throughput screening), reduction reaction pathways from theoretical insight, electrolytes choice, and electrolyzer/reactor engineering (Duarah et al., 2021; Fan et al., 2018; Gao et al., 2020; Jin et al., 2021a; Pappijn et al., 2020; Sa et al., 2020; Ye et al., 2021). However, these works of literature are not much focused on the direct utilization of CO_2 from the air pollutant as a feeding gas. As for the research in NO_xRR that only started a few years ago (Wan et al., 2021), the availability of a comprehensive review is lacking. Considering the concentration of CO_2 and NO_x pollutants are predicted to increase significantly, a detailed discussion on key technology of upcycling these pollutants into valuable chemicals *via* an electrochemical process is urgently needed. Compared to previous reviews that usually separate CO_2RR and NO_xRR studies, here we systematically review both together into point-by-point cases that we believe will be useful and helpful in the development of electrocatalytic reactors on an industrial scale, with a focus on electrocatalysts and reactor designs toward highly selective electrochemical conversion of the desired products. We provide a review to present the latest developments on upgrading CO_2 into C_1 commodity chemicals (e.g., CO, HCOOH, CH_3OH, and CH_4) and common C_2 products (C_2H_5OH and C_2H_4); and NO_x into NH_3. A perspective from the life cycle and techno-economic analyses is thus provided to claim the feasibility of the technology in actual scale implementation, as paper reviews in the field of CO_2RR and NO_xRR rarely discuss these aspects. Finally, to anticipate the growing interest in these emerging technologies, the remaining challenges and future opportunities of the upcycling route of waste into chemicals are highlighted.

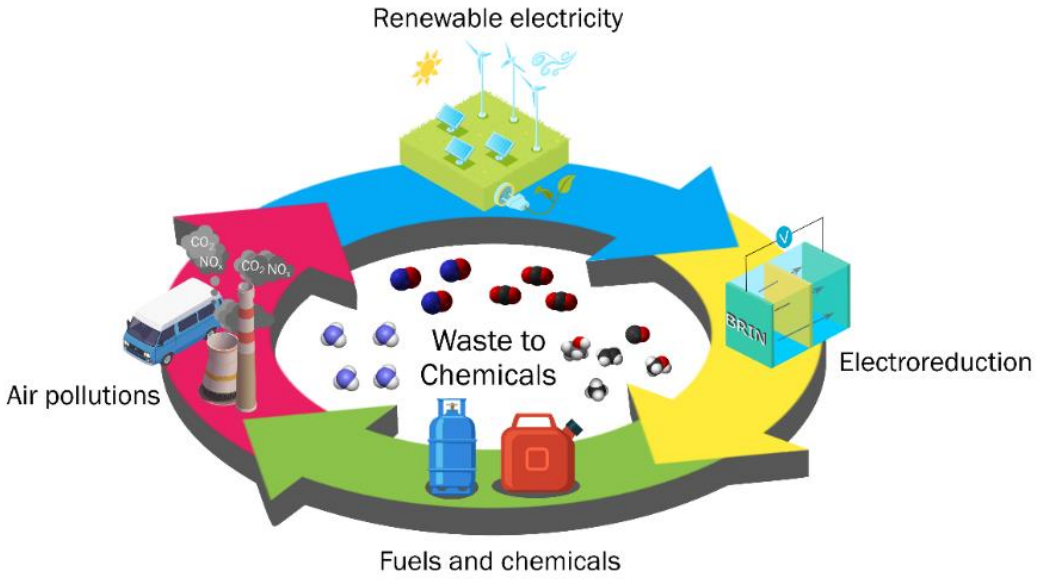


Fig. 1. Schematic representation of upcycling air pollutants into fuel and chemicals *via* electrochemical reduction technology enabled by renewable electricity sources.

2. Electrochemical reduction of CO_2

CO_2 reduction reaction *via* electrochemical process (CO_2RR) is among emerging technologies of direct utilization of CO_2 pollutants to transform them into a series of valuable chemical feedstocks being CO, HCOOH, CH_3OH, and CH_4 for C_1 products and such CH_3COOH, C_2H_4, C_2H_5OH, and C_3H_7OH for C_{2+} products (Amrillah et al., 2022; Handoko et al., 2018). The CO_2RR process often produces multiple chemicals due to the adjacent thermodynamic potentials for the important CO_2RR half-reactions in an aqueous electrolyte under standard conditions (1.0 atm, 25°C, and pH = 7.0), as listed in **Table S1** (see Supplementary Material†). Developments are, therefore, directed toward electrocatalysts and system designs to enhance the product selectivity of the desired products.

In an electrochemical conversion process, selectivity for converted products is represented by the Faradaic efficiency (FE). Low FE in the CO_2RR will increase the cost of product separation because many chemicals are generated simultaneously. Research works for CO_2RR have achieved nearly 100% for CO and HCOOH, whereas the FE of CH_3OH, C_2H_4, and C_2H_5OH are at ~85%, ~80%, and ~50%, respectively (Jin et al., 2021b). Although C_{2+} products have a higher energy density, multiple CO_2 adsorptions and proton-electron transfer processes on the catalyst surface

are required to generate longer chain hydrocarbons, and therefore, the selectivity for those C_{2+} products is relatively low. Considering this, the actual implementation of industrially converting CO_2 pollutants into C_{2+} products should take more capital and operational costs for CO_2 capture, conversion, and product separations. **Fig. 2** shows a comparison of CO_2RR products from the market prices, minimum costs of electricity per kg, and revenues generated per mole of electrons consumed. CO and CHOOH do not take much electrical energy according to their minimum electricity costs, as the CO_2 reduction pathway is relatively straightforward. Meanwhile, C_{2+} products that require more electron transfers during the CO_2RR result in much higher electricity costs. Multiple single-step reactions are necessary for the CO_2RR to C_{2+}, further affecting sluggish kinetics and high overpotential. According to the findings, electrochemical reduction of CO_2 pollutants on an industrial scale is most economically and technically feasible through electrocatalytic conversion into CO and HCOOH. The economic analysis will be further discussed in the later section.

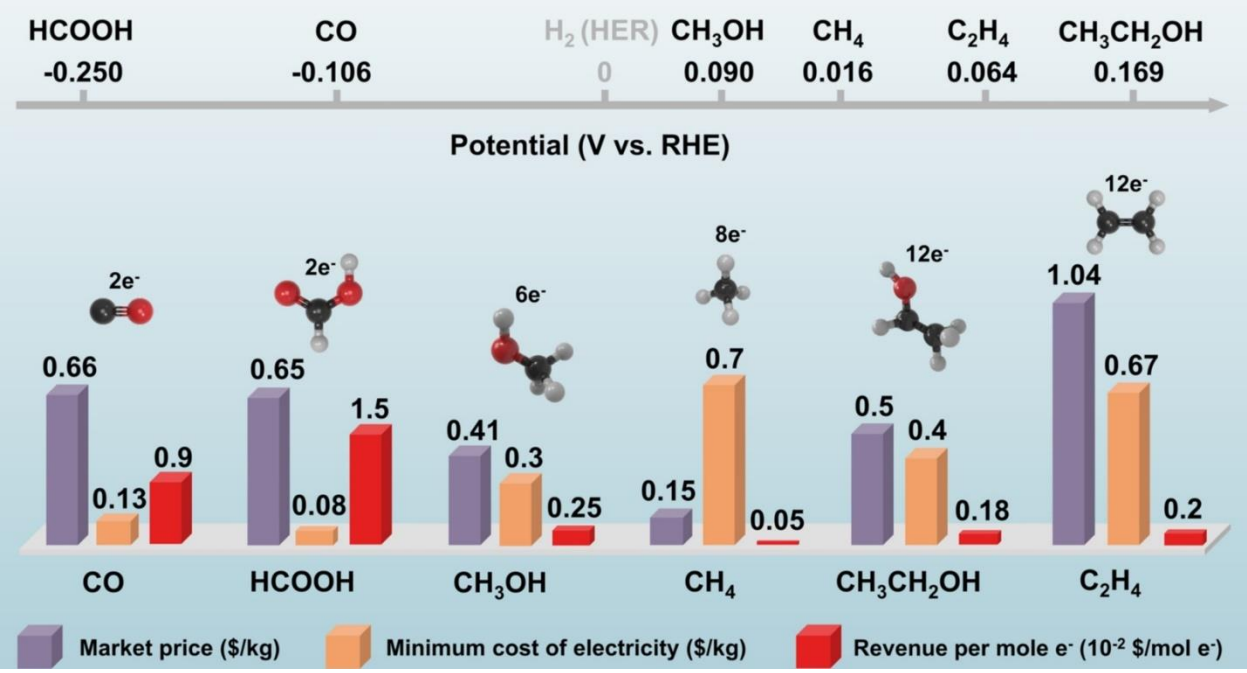


Fig. 2. Economic analysis of products in terms of their market prices, minimum costs of electricity per kg, and revenues generated per mole of electrons consumed for each (labeled in bottom panel). The market prices of common CO_2RR products come from the 2017 US commodity price. Adapted from (Jin et al., 2021b), with permission from Wiley.

2.1 Electrochemical CO_2 conversion into C_1 chemicals

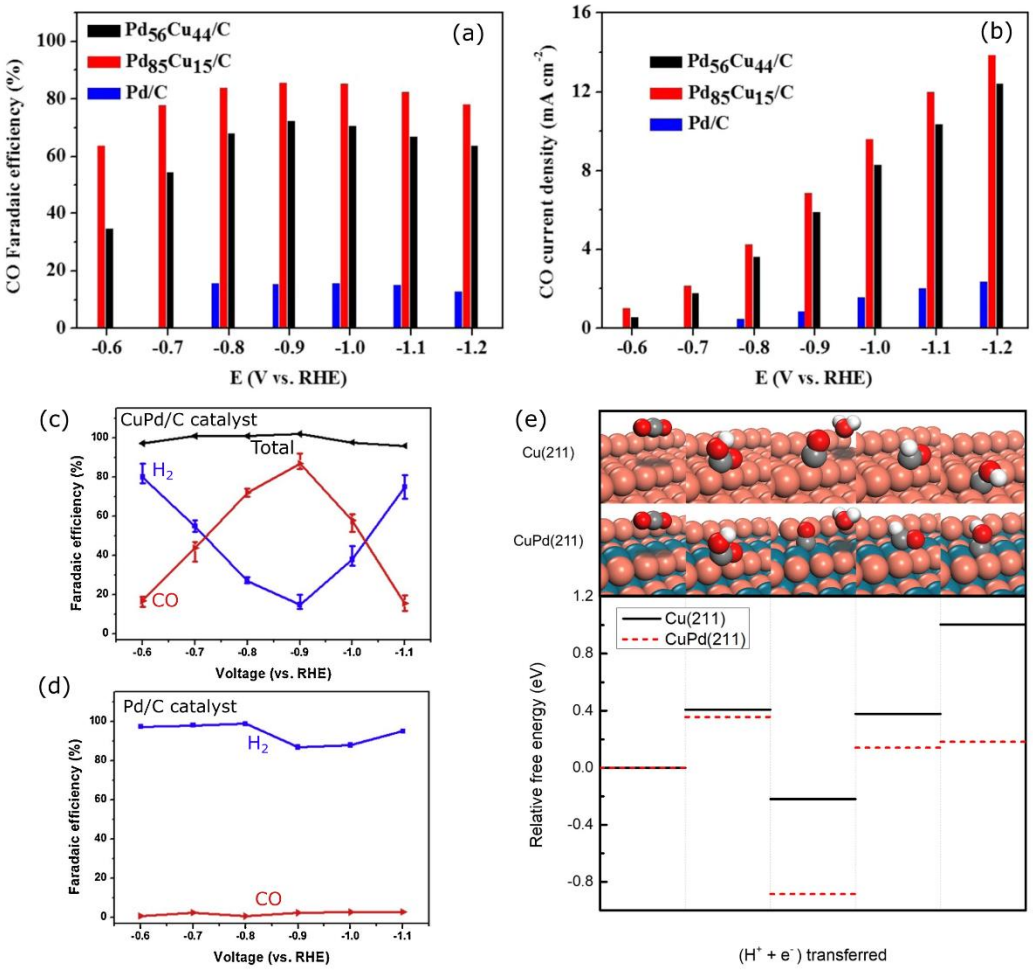
CO, HCOOH, CH_3OH, and CH_4 are the major products in C_1 chemicals produced by the CO_2RR. While the traditional CO_2-to-C_1 chemical conversion is usually achieved *via* thermal catalysis at a high temperature and involves complicated steps, the CO_2RR to C_1 molecules in aqueous electrolytes can be performed at low and moderate temperatures. It is thermodynamically favorable to reduce CO_2 electrochemically. But due to the competing HER and the multi-electrons and protons transfer processes, the CO_2RR can proceed to many possible reaction pathways that lead to the diversified generated liquid chemicals and gases. Thus, low product selectivity is a significant challenge in realizing the industrial relevance of electrochemical CO_2-to-C_1 chemicals. As selectivity control is a critical aspect of CO_2RR, we discuss the recent development and strategies to yield high selectivity of major C_1 chemicals from CO_2RR.

Carbon monoxide (CO)

CO is a substantial chemical feedstock in the chemical industry for syngas production (mixing with H_2), methanol generation, acetic acid production (through the methanol carbonylation process), and hydrocarbon chemicals synthetic (*via* the Fischer–Tropsch method). Therefore, it is essential to perform a catalytic study of tuning selectivity toward CO. Noble metal catalysts, such as Pd nanoparticles, generally showed a significant catalytic performance to electrochemically reduce CO_2 to CO with FE of about >95% depending on the applied potential (Jin et al., 2021b). It is possible to rationalize this product selectivity switch by using potential-induced and intermediate-induced active phase transitions under controlled reaction conditions. Apart from noble metal catalysts, the use of transition metal catalysts such as Ag, Ni, Fe, Co, Zn, Sn, and Se is also hopeful for CO production from CO_2RR (Fine et al., 2010; Ham et al., 2017; Mahyoub et al., 2019; Rosen et al., 2015).

Adding second metals to the metal catalyst can further improve CO production. Inspired by the concept of nano-alloying catalysts, Yin and co-workers (Yin et al., 2016) developed palladium-copper (PdCu) bimetallic electrocatalysts for the highly selective CO_2RR to CO. Among the tested catalysts, $Pd_{85}Cu_{15}$ displayed the highest FE of 86% at -0.89 V *vs.* RHE, a current density of 6.9 mA cm^{-2}, and mass activity for CO production of 24.5 A g^{-1}, which was significantly higher than PdNP catalysts (**Fig. 3** (a-b)). The presence of low-coordination sites of Cu element

over Pd metal was responsible for the highly selective CO production, as suggested by EXAFS and CO TPD-MS studies (Yin et al., 2016). Therefore, to achieve high FE and enhance CO_2 reduction activity, the controllable size and composition of the bimetallic nanoparticles are critical. A study revealed that Pd-Cu, with a ratio of 1:1, achieved the highest FE over 87% at -0.9 V *vs.* RHE, while only H_2 was produced with only Pd catalyst (**Fig. 3** (c-d)) (Mun et al., 2019). From density functional theory (DFT) calculations, when alloying with secondary metals, the energy barrier for the CO* protonation step increases, suppressing the CO_2 reduction to various hydrocarbon products (**Fig. 3** (e)). In CuIn bimetallic catalysts, neighboring Cu's adsorption properties were disturbed by In, which is preferentially located on edge sites rather than corner or flat sites (Rasul et al., 2015). Other important examples of bimetallic electrocatalysts for highly selective CO_2 conversion to CO are Cu_2Cd (Wang et al., 2018), AgIn dendrite (Park et al., 2017), bimetallic palladium complex (Raebiger et al., 2006), bimetallic Ag (Mahyoub et al., 2019), CuIn (Rasul et al., 2015), and so on.



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211 **Fig. 3.** CO_2 reduction activity over PdCu/C and Pd/C catalysts in CO_2-saturated 0.1 M $KHCO_3$
212 solution. (a) FE and (b) current density for CO production. Adapted with permission from (Yin et
213 al., 2016) Copyright 2016, Elsevier. FE CO of (c) CuPd NP/C and (d) Pd NP/C. (e) Reaction
214 pathway for CO production on the Cu(211) and CuPd(211) surfaces and the corresponding free
215 energy diagram of CO_2RR on Cu(211) and CuPd(211) surfaces. Adapted with permission from
216 (Mun et al., 2019). Copyright 2019, Elsevier.

217

218 Efforts are also being made to develop non-noble-metal catalysts and low-cost metal-free
219 materials. Researchers have reported metal-free N-doped carbon nanofibers and N-doped carbon
220 nanotubes (NCNTs) electrocatalysts for CO_2RR to CO (Kumar et al., 2013; Wu et al., 2015), with
221 the FE of CO reaching 98% and 80%, respectively. Nanoporous carbons especially have the
222 potential to be attractive electrocatalysts for the CO_2RR. The CO_2 capture capability of porous

carbonaceous materials has already been demonstrated in which the surface adsorption of CO_2 could enhance the reduction process. It is also possible to expand and manipulate abundant carbon materials' catalytic properties by various surface modification methods or doping with heteroatoms. Compared to metals, the electrocatalytic stability of carbon surfaces is expected to be greatly improved since they are resistant to poisoning during reduction. The confined space provided by the developed porosity in the carbon-based porous catalysts may dramatically alter the reduction processes. It was demonstrated that S-doped and dual S,N-doped polymer-derived carbons (Li et al., 2016), N,S dual-doped carbon nanoweb (Han et al., 2020), and Zn,N-codoped graphene (Z. Chen et al., 2018) could stabilize the $CO_2^{\bullet-}$ and COOH* intermediates, promoting the high selectivity of CO formation, thus achieving FE >90% (Z. Chen et al., 2018). Other developed catalysts for the promotion of CO formation include metal-organic frameworks (MOFs) (Dong et al., 2018), metal sulfides (Qin et al., 2019), metal oxide core-shell structures (Li et al., 2017), etc. Aside from the developed electrocatalysts, the selectivity of CO is governed by the reaction conditions such as reactor design, electrolyte compositions, operating temperatures, and feeding gas compositions (Bhargava et al., 2020; He et al., 2020; Kim et al., 2016; Krause et al., 2020).

Formic acid (HCOOH)

Chemical industries and renewable energy sectors rely heavily on formic acid (HCOOH), a key feedstock for producing various chemicals. Different organic chemicals, including aldehydes, ketones, carboxylic acids, and amides, can be synthesized by formic acid derivatives such as formate esters (Lu et al., 2014). HCOOH can also be used to generate electricity, as a direct fuel for automobiles, and in methanol fuel cells, due to its electrochemical oxidation potential at Pt–Ru/C electrodes. HCOOH in the conventional fossil-based process is produced by combining CH_3OH and CO to generate $C_2H_4O_2$, then hydrolyzing it to produce HCOOH (Russell et al., 1977). HCOOH can potentially be a future hydrogen storage compound as it is catalytically decomposed into CO_2 and H_2 in a suitable condition (Yoo et al., 2016). The type of electrocatalyst, electrode potential, reactant, and electrolyte all play a vital role in the product selectivity and efficiency of CO_2RR. Researchers have proposed a variety of strategies for making HCOOH efficiently through CO_2RR (Wenjun Zhang et al., 2018; Zhao et al., 2021). Over the past few years, substantial research has been aimed at developing highly efficient electrocatalysts, electrolytes, and reactor designs for HCOOH production.

There have been many successive studies in finding highly efficient catalysts for a single product of HCOOH, including metal electrocatalysts (Duarah et al., 2021; Feaster et al., 2017; Kortlever et al., 2015a), metal alloys (Kortlever et al., 2015b; Kwon et al., 2019; Li et al., 2020; Ren et al., 2020), metal oxides (Wu et al., 2018), carbon allotropes (Natsui et al., 2018), metal-organic frameworks (MOFs) (Hwang et al., 2020; Zhao et al., 2021), etc. Like many electrocatalytic processes, noble metals are primary and practical electrocatalysts for CO_2 reduction because of their strong catalytic activity. Their cost of production effectuates the price of the chemicals produced by CO_2RR, which may need to be more competitive with conventional production. Metal alloys are more efficient CO_2 catalysts for HCOOH formation because the interfacial site between two metals is highly reactive, making the HCOOH pathway significantly energy favorable. For instance, $Zn_{0.95}In_{0.05}$ exhibited remarkable CO_2 electrocatalytic activity with the FE of HCOOH reaching 95% at 1.2 V *vs.* RHE and with an HCOOH production rate of 0.40 mmol h^{-1} cm^{-2} (Kwon et al., 2019). The critical point to producing formic acid from CO_2 with high selectivity at low overpotentials is to avoid surface catalyst poisoning by CO, which can rapidly suppress the catalytic activity (Kortlever et al., 2015b).

Theoretical and high-throughput screening can guide and accelerate the development of efficient CO_2 electrocatalysts to prevent laborious work on trial-error experiments (Hitt et al., 2021; Steinmann et al., 2022; Yoo et al., 2016), specifically toward selective production of HCOOH. In this case, employing the BEEF–vdW functional in DFT calculations to describe the physisorption and chemisorption properties of CO_2 molecules on transition-metal surfaces resulted in accurate energetics of CO_2RR to HCOOH (Yoo et al., 2016). Of 27 investigated metals, Pb and Ag were identified as the most promising selective catalysts for HCOOH production *via* CO_2RR, which could suppress HER, as shown in **Fig. 4**. The approach may widely be applied to other materials to spur the computational catalyst screening for CO_2RR to HCOOH that potentially lead to the discovery of more abundant, efficient, and selective catalysts enabling CO_2RR technology (Hitt et al., 2021).

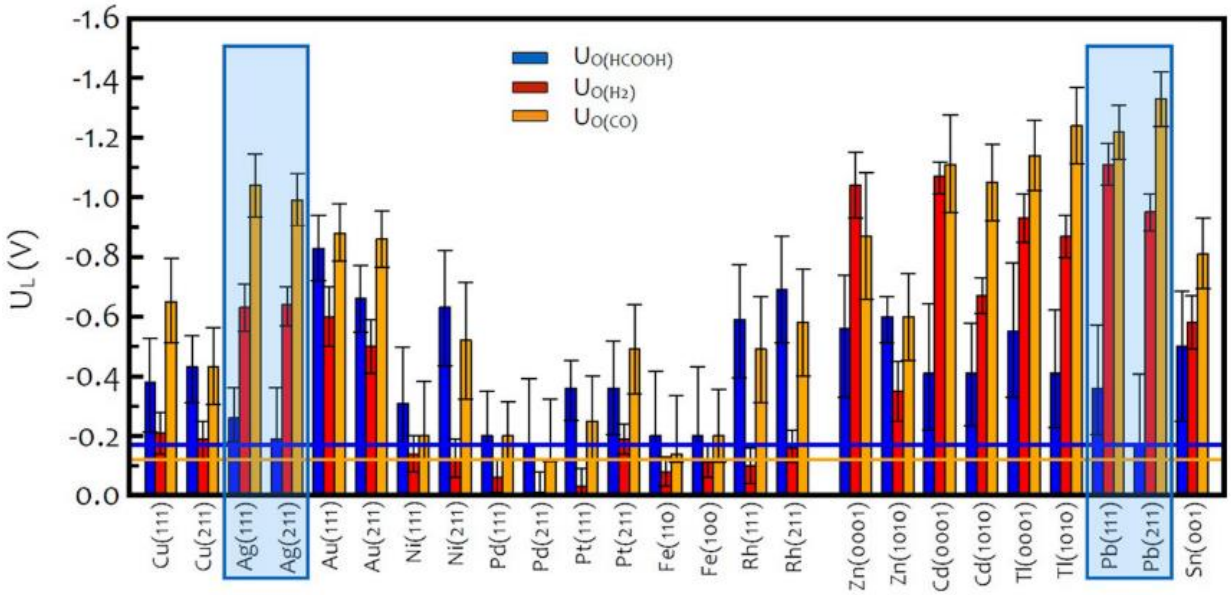

Fig. 4 Theoretical limiting potentials (at pH 0) for the CO_2RR to HCOOH (blue bars), HER (red bars), and CO_2RR to CO (orange bars) on various metal surfaces. The blue and orange lines indicate theoretical equilibrium potentials for HCOOH (−0.17 V *vs.* RHE) and CO (−0.12 V *vs.* RHE), respectively (note that the equilibrium potential for hydrogen evolution is 0 V *vs.* RHE). Reprinted with permission from (Yoo et al., 2016). Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The operating parameters such as current density, cathode to anode area ratio, pH, scan rate and nature of the anode, and supporting electrolytes were studied thoroughly, aiming to find the best conditions for HCOOH production through CO_2RR (Ramdin et al., 2019a). It is suggested that high-pressure CO_2 feeding (15–30 bar) enabled high production of HCOOH (up to 0.46 mol L^{-1}) (Scialdone et al., 2016). Different aqueous electrolytes are identified, affecting the CO_2RR for HCOOH promotion. Room temperature ionic liquids (RTILs) are advantageous and promising CO_2RR-supporting electrolytes for their high CO_2 solubility, good ionic conductivity, and wide potential window. The CO_2RR in the presence of RTIL-containing electrolytes has been extensively conducted. For instance, Pb or Sn electrode was used to electrocatalytically reduce CO_2 into HCOOH with partial current density for HCOOH reaching 37.6 mA cm^{-2} at a FE of 91.6% in [Bmim]PF_6/AcN or [Bmim]BF_4/AcN mixtures with different H_2O content (**Fig. 5** (a-f)) (Zhu et al., 2016). The conductivity of the electrolyte at the electrode/IL interface and weak cation-

anion interactions of the small size of IL aggregates are favorable for improving the efficiency of the CO_2RR (Zhu et al., 2016). The ternary electrolytes consisting of [Bzmim]BF_4 (14.7 wt%), H_2O (11.7 wt%), and acetonitrile have enhanced the CO_2RR over PbO_2 electrodes to promote HCOOH formation with high FE (95.5%) and high current density (40.8 mA cm^{-2}) (Wu et al., 2018). The use of 1-ethyl-3-methylimidazolium dicyanamide ([Emim][$N(CN)_2$]) electrolyte showed a FE of 81.9% toward the formation of HCOOH over Sn metal electrodes, as depicted in **Fig. 5** (g-h) (Zhang et al., 2017). In addition to what has been mentioned, electrochemical reduction systems have been introduced to increase mass transfer and solubility of CO_2 into electrode surface, such as gas diffusion electrodes (GDEs) (Wang et al., 2014), gas-phase $^{12}CO_2$ (Lee et al., 2015), continuous semi-micro reactor (Sinha et al., 2020), and various membranes (Ramdin et al., 2019b; Yang et al., 2017). These successful reactors have moved CO_2RR technology toward practical development by stabilizing cell performance and lowering the production cost barrier.

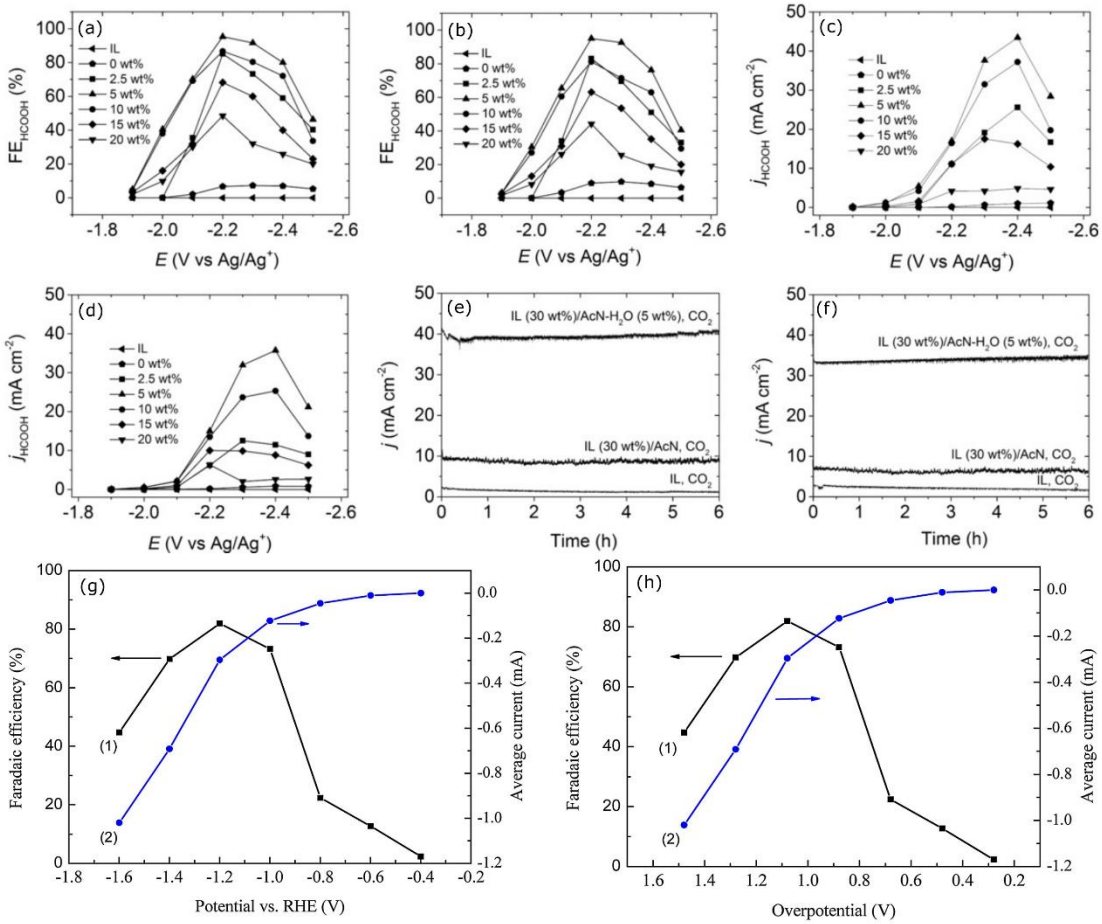

Fig. 5. Effect of current density and FE using [Bmim]PF_6 (30 wt %)/AcN-H_2O electrolytes with different H_2O contents. FE of HCOOH on (a) Pb and (b) Sn electrodes; partial current density of HCOOH on (c) Pb and (d) Sn electrodes; the dependence of current density over time on (e) Pb and (f) Sn electrodes. Adapted with permission from (Zhu et al., 2016). Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Variations in the FE of formic acid (g) and average current (h) as a function of the applied electrolysis fixed potential. The electrolyte is a CO_2-saturated 0.5 M [Emim][$N(CN)_2$] aqueous solution, and the total electrolysis time for each experiment is 2 hours. Reproduced with permission from (Zhang et al., 2017). Copyright 2017, Elsevier.

Methanol (CH_3OH)

CH_3OH has many applications, being raw compounds to commodity chemicals like aromatics, ethylene, propylene, methyl methacrylate, and others, as depicted in **Fig 6**. A further advantage of CH_3OH is that it is liquid at ambient temperatures and pressures, making it easy to store and transport; also, it can be directly utilized in fuel cells. The capacity of CH_3OH production is about 110×10^6 tons/year, which uses 2×10^6 tons of CO_2. An energy-efficient, selective, and zero-waste method for converting CO_2 into CH_3OH would be highly desirable. The CO_2RR into CH_3OH is believed to revolutionize the 'methanol economy.'

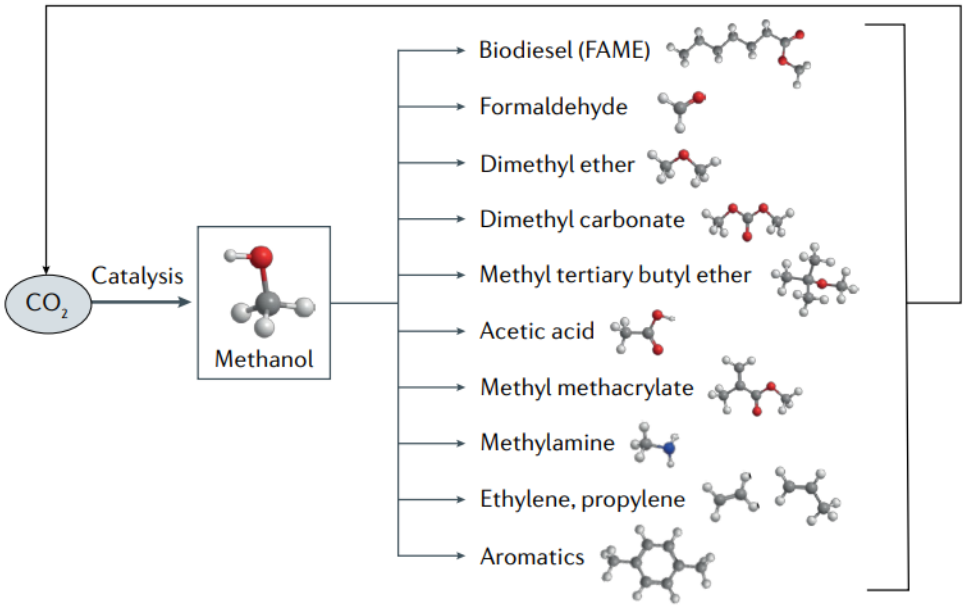

Fig 6. The carbon cycle of a platform molecule for the chemical industry, CH_3OH. FAME means fatty acid methyl ester. Reproduced with permission from (Navarro-Jaén et al., 2021). Copyright 2021, Nature Publishing Group.

The CO_2RR to CH_3OH has been investigated using a variety of metal-based electrocatalysts, of which Cu-based catalysts are benchmark electrocatalysts, but they have often been found to be inefficient and low-active. Alloying with metals may improve Cu-based electrocatalysts (Hirunsit et al., 2015). Theoretically, HCOOH production can be efficiently catalyzed on Cu_3Pt, Cu_3Ni, Cu_3Co, and Cu_3Rh surfaces. Meanwhile, CH_3OH production is favorable on Cu_3Pd and Cu_3Pt surfaces, yet they show high overpotential (~0.7 V) (Hirunsit et al., 2015). The performance of Cu_xPd_y aerogel electrocatalysts was experimentally assessed in aqueous 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) electrolyte. The aerogel catalysts showed a charge density of 31.8 mA cm^{-2} over 24 hours, at which CH_3OH FE of 80.0% was achieved, with the structure of the aerogel being maintained intact. Fine inorganic network structures with high porosity contribute to the excellent catalytic activity of the Cu-Pd alloy on the surface. As Pd and Cu interact *via* charge transfer, Cu-Pd alloys do not form excessively strong bonds, resulting in less CO and CH_3OH production inhibition. Therefore, Pd and Cu may assist in CH_3OH production in the presence of CO (Lu et al., 2018). Nanoparticles as catalysts result in

high electrochemically active surface areas and provide abundant active sites in the corner, edge, and basal planes, coordination numbers, local electronic structures, facets, and defects. A non-metal boron phosphide (BP) nanostructured catalyst has been investigated in 0.1 M $KHCO_3$. This catalyst exhibited a high CH_3OH FE of 92.0% at −0.5 V *vs.* RHE and a conversion rate of 127.5 μg h^{-1} $mg^{-1}_{cat.}$ at −0.6 V *vs.* RHE with strong electrochemical stability (Mou et al., 2019). B and P could synergistically promote the CO_2 molecules' binding and activation on BP (111), while the rate-determining step for CO_2RR was dominated by *CO + *OH to *CO + *H_2O that could selectively induce CH_3OH generation (Mou et al., 2019). In a theoretical study, the key parameter of CH_3OH selectivity was the formation favorability of CH_2OH* intermediate associated with the preference of CH_2OH* protonation at the C atom over the O atom (Hirunsit et al., 2015).

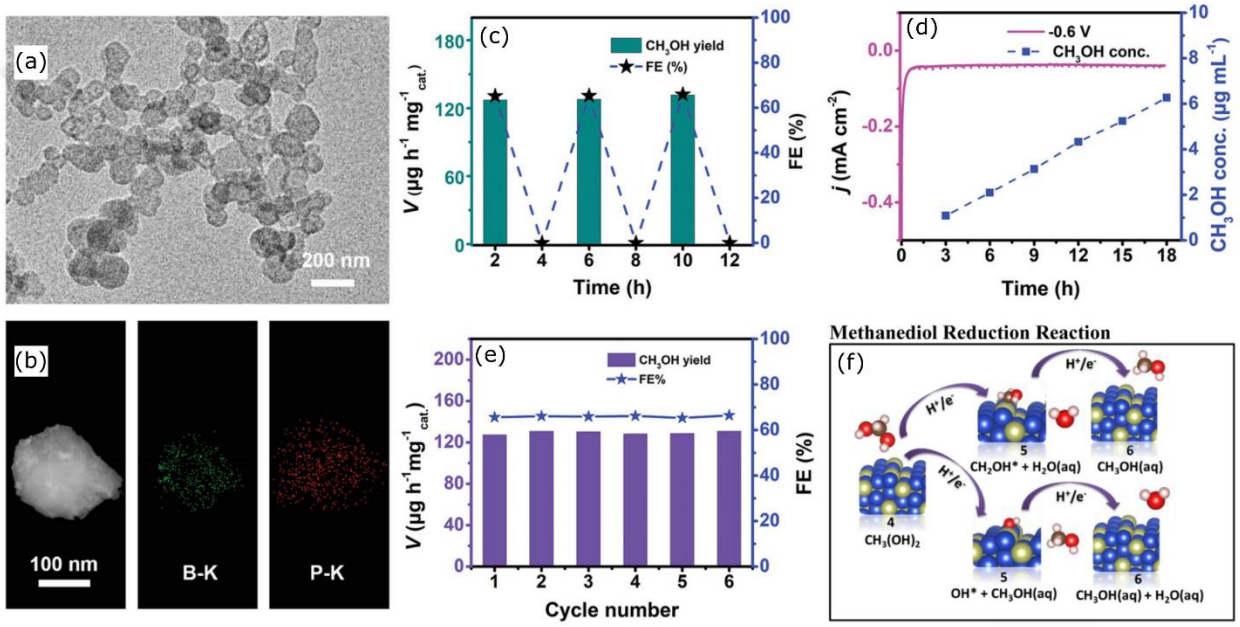

Fig. 7 (a) TEM and (b) STEM image and corresponding EDX elemental mapping images for boron phosphide (BP). (c) CH_3OH yields and corresponding FEs for BP/CP with intervals of 2 h cycles in CO_2- and Ar-saturated electrolytes. (d) The total current density (left axis) and CH_3OH production (right axis) of BP/CP at −0.6 V for 18 h in CO_2-saturated 0.1 M $KHCO_3$. (e) CH_3OH yields and FEs at −0.6 V for recycling tests in 0.1 M $KHCO_3$. Reprinted with permission from (Mou et al., 2019). Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (f)

The reaction pathways for methanediol reduction to methanol. Reproduced with permission from (Hirunsit et al., 2015). Copyright 2015, American Chemical Society.

Researchers have been inspired to combine metals with carbon materials to make electrocatalysts because of the high activity of porous materials. Since carbon materials have a high surface area and electrical conductivity, they can stabilize high metal loadings and promote electron transfer to and from metal catalyst sites. Materials with tunable porosity, such as MOFs, are the primary choice for adsorbing, separating, activating, and electroreducing CO_2 owing to their highly porous structure, high conductivity, large surface area, and controllable structural features that are supported by many theoretical calculations and simulations (Zhao et al., 2021). Recently, their composites and derivatives for CO_2RR into CH_3OH have been reviewed (Al-Rowaili et al., 2018). CH_3OH can be produced with high FE using zinc dendrites pulse-deposited on silver foam (Low et al., 2019), anodized titanium electrodes (Teh et al., 2021), hierarchical Pd/SnO_2 nanosheets (Wuyong Zhang et al., 2018), MXenes (Amrillah et al., 2022; Handoko et al., 2019; Lim et al., 2020; J. Liu et al., 2020), and many more. Also, organic solvents or anionic liquids supporting electrolytes have been capable of realizing the six protons-electrons transfers for selective CH_3OH production. These media are noted for their higher CO_2 solubility and ability to stabilize charged intermediates.

Methane (CH_4)

Of generated chemicals from the CO_2RR, methane (CH_4) is an attractive chemical and intermediate for its advantages: (i) high energy density (~50 MJ kg^{-1}), (ii) produces more heat and energy compared to other hydrocarbon fuels (e.g., gasoline and diesel), (iii) emits significantly less CO_2 which contributes to a healthier atmosphere, and (iv) efficient energy carriers from excessive renewable electricity. Cu is generally a promising electrode for CO_2RR to CH_4. According to the theoretical calculations, the shifted d-band center of the Cu site causes a reduction of $*CH_2O$ and $*CH_3O$ intermediates formation energies, which is become the potential-determining step of CO_2 reduction reaction to CH_4 (Y. Zhang et al., 2022a). Nevertheless, as with every electroreduction CO_2 catalysis to other products, CO_2RR to CH_4 encounters similar problems, including the high negative potential required to activate the stable CO_2 molecules

(≈−1.9 V *vs.* NHE). The need for noble metal catalysts to reduce the overpotential is undeniable to this extent, but their low abundance makes them unsustainable solutions. The subsequent protons/electrons couple reactions after CO_2 activation are also not specific, resulting in a mixture of gaseous and liquid products (Alqahtani et al., 2018). However, the issue related to the scarcity of noble metals is not the main challenge for CO_2RR to CH_4 as several kinds of promising and efficient catalysts have been well explored, such as cobalt phthalocyanine (CoPc) and zinc–nitrogen– carbon (Zn-N-C) tandem catalyst (Lin et al., 2020), porous hollow fiber electrodes (Alqahtani et al., 2018), single-atom catalysts (Back and Jung, 2017; Cai et al., 2021; X. Liu et al., 2020), molecular catalysts (Ahmed et al., 2020; Nganga et al., 2021), metal alloys (Ismail et al., 2020; Wang et al., 2020), metal oxides (Cai et al., 2022; Wang et al., 2021), MXenes (Amrillah et al., 2022), metal nanowires (Liu et al., 2018), MOFs (Zhao et al., 2022), etc.; all of which come with their risk-benefit performances. For instance, noble metal single-atom catalysts generally possess the lowest overpotential, highest FE, and most stable properties, yet their costly production is unfavorable for producing chemicals at competitive prices.

Several reviews on electrocatalysts for CO_2RR to CH_4 have been recently published (Amrillah et al., 2022; Lim et al., 2014; Zheng et al., 2021), but we are particularly interested in emerging microbial electrocatalysis (MES) technology that is recently gathered much attention as this process allows to boost CH_4 production significantly. While CH_4 production *via* anaerobic digestion (AD) has been a developed method, microbial electrochemical CO_2 into industrially renewable fuels shows a future promise for CCUS since it uses regenerative, environmentally friendly, and abundant microbial catalysts that have good selectivity for desired products (e.g., CH_4, formate or biocomplex molecules) with a high generation rate (Chu et al., 2020; Rabaey and Rozendal, 2010; Fang et al., 2022, 2021). In this topic, biosystem hybridization consisting of inorganic HER catalysts to generate H_2 and microbial CO_2 catalysts in the form of biofilm has been attempted to produce CH_4 from CO_2 reduction. Microbial catalysts consisting of the biocompatible photo(electro)chemical HER and *M. barkeri* have reduced CO_2 to CH_4 using the in situ generated H_2 (Nichols et al., 2015). Alqahtani et al. (Alqahtani et al., 2018) coupled porous hollow fiber nickel electrodes acting as HER electrocatalysts with enriched methanogenic archaea community. The porous architecture also played as a gas-transfer membrane for delivering CO_2 to CO_2-reducing methanogens (*Methanobacteriales*) on the cathode, as shown in **Fig. 8**. The developed microbial electrosynthesis cell system achieved FE_{CH4} of 77% at –1 V *vs.* Ag/AgCl with

a production rate of CH_4 is 140 ± 13 mmol m^{-2} d^{-1}. Huang et al. (Huang and Hu, 2018) used *M. maripaludis* as a strain of methanogen, which enabled CH_4 production at a rate of 0.01 mmol d^{-1} mL^{-1} at a cathodic potential of −1.4 V *vs.* Ag/AgCl. Interestingly, MES can be potentially paired with renewable electricity from wind or solar. In the case of using solar electricity, MES performs in an equivalent manner to natural photosynthesis that uses water, sunlight, and CO_2 to produce hydrocarbon chemicals. A more detailed discussion on the microbial electrosynthesis can be found elsewhere (Fang et al., 2022, 2021).

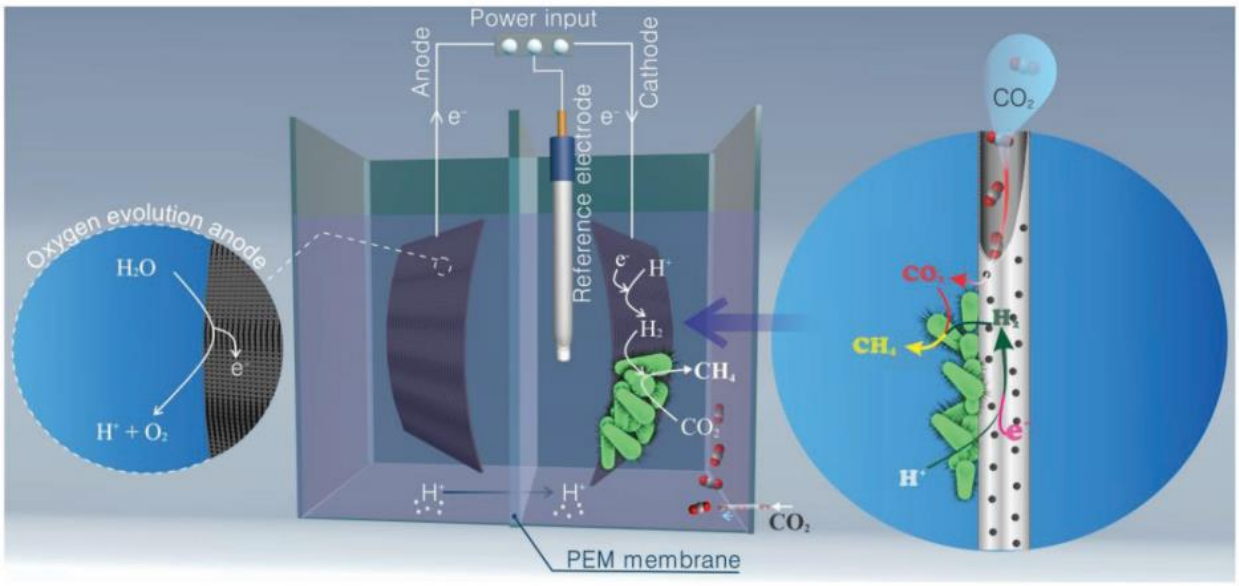

Fig. 8. A schematic of a microbial electrosynthesis (MES) reactor that replaces a conventional submerged flat cathode with an electrically conductive, catalytic, and porous hollow-fiber (CCPHF) cathode. The CCPHF cathode acts as an inorganic electrocatalyst for hydrogen generation from proton reduction and a gas-transfer membrane for direct CO_2 delivery to CO_2-fixing hydrogenotrophic methanogens (biological catalyst) on the cathode through the pores of the hollow fibers. The water oxidation reaction at the anode supplies the electrons for the HER at the cathode of MES. Hydrogenotrophic methanogens utilize the hydrogen generated at the cathode as a source of reducing equivalents for converting CO_2 to CH_4. Reproduced with permission from (Alqahtani et al., 2018). Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.2 Electrochemical CO_2 conversion into C_{2+} chemicals

The C_{2+} product synthesis with two or more carbon atoms can also be achieved by electrochemically reducing CO_2 *via* C–C coupling and chain growth, as it has a high energy density and can be used as transportation fuel or basic chemicals. The product distribution among C_{2+} products would be determined by selectivity control after the C–C coupling step. Although CO_2RR can reduce CO_2, its selectivity toward specific products is poor. A mechanistic understanding of full reaction pathways is crucial for producing a highly selective single C_{2+} product. This chapter discusses selective CO_2 reduction into several common C_{2+} chemicals such as ethanol, ethylene, etc. We observed that for any given C_{2+} product, many subsequent reaction steps are involved in the growth of the C–C coupling, making tandem catalysis an excellent strategy for achieving high selectivity. Tandem catalysis uses more than one catalyst to promote two or more mechanistically distinct reaction steps.

Ethanol (C_2H_5OH)

The CO_2RR into multi-hydrocarbon products, such as ethanol, has large-scale yields that eventually receive significant research and commercial interest. Electroreduction of CO_2 in the solution could promote proton-electron transfer, depending upon its different pathways, numbers of protons and electrons transferred, and various catalytic products, e.g., C_1 products: carbon monoxide (CO), methanol (CH_3OH), formic acid (HCOOH), methane (CH_4), and C_2 products: ethylene (C_2H_4), ethanol (C_2H_5OH) and others (Lu et al., 2022). Despite their synthesis being relatively more complex compared to C_1 products, as more significant amounts of protons are required during the process of CO_2 conversion, it is found that the C_2 products from CO_2RR are more valuable. More specifically, the production efficiency for ethanol still faces significant challenges, such as the limitation of selectivity under high current operation, low stability, and poor catalytic activity, which affect low-grade chemical feedstock (Wang et al., 2022). Many attempts have been conducted to overcome this. One found a new catalytic material that exhibited excellent *CO adsorption to efficiently trigger asymmetric C–C coupling to stabilize ethanol intermediates (Wang et al., 2022). An introduction of a single atom on the catalytic material was thought to optimize the coordinated number and oxide state of surface sites (Wang et al., 2022) of catalytic material for CO_2-ethanol conversion. A new silver–modified copper–oxide catalyst

(Cu$_2$O/Ag) could achieve a significant FE of 40.8% for EtOH production under which the high current with a partial current density of 326.4 mA cm^{-2} at −0.87 V *vs.* RHE is operated (Fig. 9) (Wang et al., 2022). In Cu-based electrocatalytic material, Cu sites at the surface could act as an electron donor, decreasing the reaction barrier in the potential-determining C−C coupling step, thus further influencing the electrocatalytic performance for ethanol production (Guo et al., 2022). Modifying the surface state of catalytic material is essential to boost electrocatalytic efficiency. Therefore, searching for a new type of catalytic material and finding a proper choice of a single atom for material decoration will be helpful in CO_2RR into ethanol.

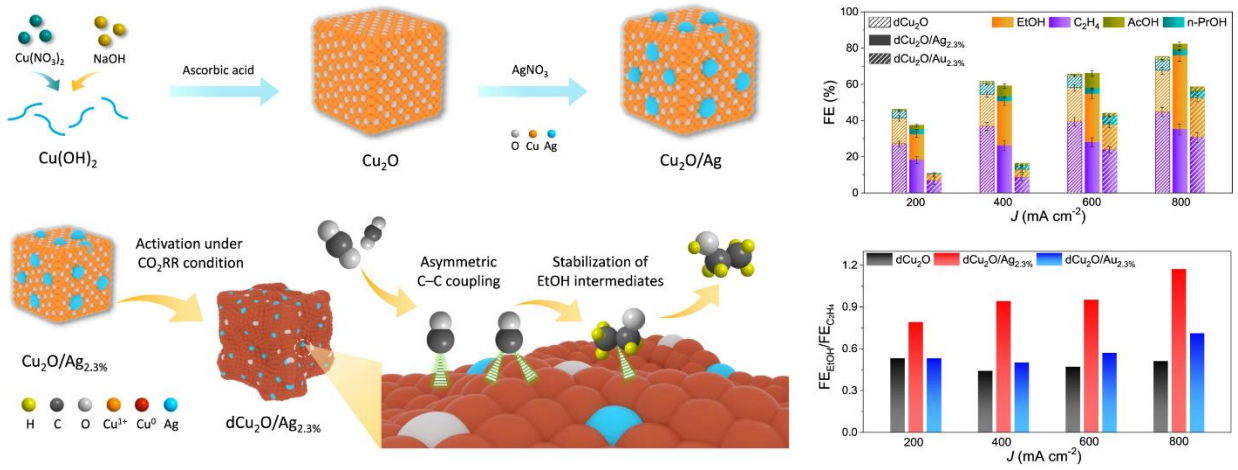

Fig. 9. Boosting electrocatalytic CO_2–to–ethanol production *via* asymmetric C–C coupling enabled by a new silver–modified copper–oxide (Cu$_2$O/Ag) catalyst. Adapted with permission from (Wang et al., 2022). Copyright 2022, Nature Publishing Group.

Internal modification of catalytic material could be an effective strategy to boost the CO_2RR into ethanol. One of those would be a structural modification of catalytic sites. A modification in the material's porosity has been explored as confining units to improve catalytic activity and overcome the leaching or aggregation of noble metal-based catalysts (Li et al., 2021). On the other hand, catalytic materials in amorphous form exhibited better catalytic performance than their crystalline counterparts due to their greater flexibility (Goldsmith et al., 2017). Modifying the dimension shapes of catalytic materials is also an excellent way to improve the catalytic performance for CO_2-ethanol conversion. Two-dimensional (2D) materials exhibit great potential in the CO_2RR for their distinctive electronic and structural properties, good electrical

conductivity, large atomic utilization, and high specific surface area than other types of low-dimensional shapes materials (Amrillah et al., 2022; J. Liu et al., 2020; Lu et al., 2022).

Moreover, boosting electrocatalytic C─C coupling in aqueous electrolytes could be optimized using a proper design of catalysts and reactors (Fan et al., 2020). A high reaction pressure during the catalytic process could enhance the bulk and interface CO_2 concentration. Reactor design could be one of such pathways to obtain a high-pressure process, as likely as a recent high-pressure reactor consisting of a stainless-steel autoclave with high-pressure CO_2 (up to 60 atm) that could lead to a tremendous enhancement in both the FE and the current density of C_{2+}. Another reactor design to generate C_{2+} oxygenated from CO_2RR is usually mixed with solutes such as $KHCO_3$ and KOH in the electrolyte for traditional H- or flow-cell reactors (Fan et al., 2020).

Ethylene (C_2H_4)

Ethylene (C_2H_4) is included in the C_{2+} product of the CO_2RR. The C–C coupling during the CO_2RR is the most critical step in stabilizing the product of the multi-carbon compound. It starts between different C-containing intermediates generated from *CO dimerization. The *CO dimer is reduced to *$OCHCH_2$, serving as the intermediate and responsible for ethylene and ethanol's selectivity. The overpotential determines the final products being a low overpotential is needed for CO and formate, and a high overpotential is important for deep electroreduction products of methane, ethanol, and ethylene (Catalysts and Qian, 2022). Likewise, in ethanol formation, a Cu-based catalyst is suitable as a pilot for electrocatalyst in CO_2 conversion into ethylene. Previous reports showed that Cu's surface condition is pivotal in determining ethylene formation (Catalysts and Qian, 2022; Jiang et al., 2021; W. Liu et al., 2022; Yano et al., 2004). Enhancing the electrocatalytic performance is a mandatory task to obtain a highly efficient conversion of CO_2 into C products, as it also applies to ethylene. Several attempts have been conducted to increase the electrocatalytic performances for CO_2 conversion into ethylene, as in surface engineering using doping and surface termination, compositing catalytic material, shape dimension modification, etc. (Cheng et al., 2017; Jiang et al., 2021; W. Liu et al., 2022; Ma et al., 2020; Qiu et al., 2021). Also, ethylene production could be enhanced by regulating the supply of different CO_2 partial pressures (Song et al., 2020).

2.3 Reactor design of electrochemical CO_2 reduction

Reactor design plays a crucial role in the efficiency and stability of the CO_2RR process. Wang's group at Rice University have significantly contributed to developing innovative reactor designs with ultrahigh mass transfer for CO_2RR. For instance The reactor consisted of a porous electrode with a high specific surface area and a microfluidic channel for the electrolyte flow (Kim et al., 2022). This design allowed for efficient mass transfer of CO_2 and reduced species to the electrode surface, leading to improved electrocatalytic activity and selectivity. In another work, the team described a scalable flow reactor for efficient CO_2RR to multi-carbon products (Fan et al., 2022). The reactor consisted of a three-dimensional (3D) printed flow-through electrode with a high surface area and a microfluidic channel for electrolyte flow. The 3D printing technique allowed for the creation of complex and high-surface-area structures that enhanced the performance of the reactor (Zhu et al., 2021; Zhu and Wang, 2021). They also reported on a scalable flow reactor for efficient CO_2RR to multi-carbon products. These works have advanced the field and paved the way for more efficient and sustainable methods of producing chemicals and fuels.

As a proof of concept, reactor design and configuration are prominent in achieving high-efficiency conversion of CO_2 into ethylene. Several designs of electrocatalytic reactors have been proposed, namely gas diffusion electrodes (GDE)-based flow cells, microchannel reactors, membrane electrode assembly, and high-pressure cells (Lin et al., 2022). The development of electrocatalysts to obtain high-efficiency conversion is aligned with the types of reactors used in ethylene production. Electrocatalysts have poor conversion ability that results in low reactions rate, thus requiring large-scale reactor volumes to expect more conversion (Pappijn et al., 2020) but then giving high-cost production consequences. Proper reactor design and configuration can support CO_2 conversion to provide high-rate reactions and yields of ethylene to decrease production costs eventually (Lin et al., 2022). The GDE-based flow cell modified with Cu-nanoparticles could boost the electrochemical reaction rate of CO into ethylene (Han et al., 2018). A recent report attempted to enhance the electrocatalytic performance while decreasing the toxicity and poisonous compounds in the electrocatalytic reactor (Daiyan et al., 2019). In the CO_2RR to ethylene, the electrode suffers a decline in its catalytic activity for reducing CO_2 to hydrocarbons due to carbon deposition. The carbon deposition can physically block active sites on the electrocatalyst surface and alter the electronic properties of the electrocatalyst, leading to changes

565 in the kinetics of the catalyzed reaction. The changes can occur through several mechanisms,
566 including carbon reduction and hydrocarbon adsorption. One of those attempts to overcome this
567 is by developing an electrolysis system of CO_2 reduction using a three-phase (gas//liquid//solid)
568 interface on a Cu-mesh electrode (Yano et al., 2004).

569

570 **3. Electrochemical reduction of NO_x to NH_3**

571 The traditional selective catalytic reduction (SCR) technology has been industrially
572 adopted for NO_x removal, in which NO_x molecules are reduced into harmless N_2 and H_2O by NH_3
573 at a temperature higher than 300^{o}C. Besides NH_3-SCR catalysts being energy-extensive and having
574 high operating costs, they also produce substantial levels of secondary pollution. Furthermore,
575 many NH_3-SCR catalysts operate at high temperatures to be well-performed. Direct capture and
576 utilization of gaseous NO_x pollutants from the atmosphere provide a new scenario for converting
577 waste to fuels and chemicals. The NO_xRR is one of the fascinating routes for NO_x-related pollutant
578 treatment and NH_3 conversion (Tursun and Wu, 2021). Commercial design of the reactor for a
579 sustainable NO_xRR to produce NH_3 on-site would be potential for economic and environmental
580 advances (Abghoui et al., 2015; Liang et al., 2022a; Niu et al., 2021). However, the NO_xRR process
581 in ambient conditions has faced significant challenges. According to Abghoui et al., the first
582 observations of NH_3 synthesis under milder conditions were reported using homogeneous catalysts
583 with tungsten, zirconium, and tantalum as the central atoms (Abghoui et al., 2015). On the other
584 hand, using heterogeneous catalysis will result in more efficient yields and allow for facile
585 isolation of NH_3 products (Abghoui et al., 2015).

586

587 **3.1 Rational design of NO_x electroreduction catalysts**

588 The century-old Haber-Bosch process has been industrially applied to synthesize NH_3 but
589 is unsustainable to employ extreme operating conditions and generate massive CO_2 gas emissions.
590 The NO_xRR is considered more eco-friendly for NH_3 production but offers low conversion
591 efficiency (Ouyang et al., 2022). Direct utilization of gaseous NO_x pollutants for the NO_xRR has
592 been exponentially proposed, encouraging new concepts for both NO_x removal and NH_3 synthesis.
593 Designing efficient catalysts for NO_xRR will significantly advance this field. While the hopes for
594 NO_xRR are high, so are the challenges (Niu et al., 2021). The NO_xRR catalysts often contain noble
595 metals such as platinum (Pt), palladium (Pd), and frequently silver (Ag) (Zhou et al., 2022), which

are scarce and high-price resources, thus significantly hampering their large-scale application (Ouyang et al., 2022). Other than noble metals, iron (Fe), cobalt (Co), nickel (Ni), and copper (Cu) are among the preferred representative metal-based catalysts commonly used for electroreduction reactions (Ko et al., 2022). However, those metals are limited on Earth and may induce other environmental pollution due to metal ion release (Ouyang et al., 2022). A series of noble-metal free catalysts in the two-dimensional (2D) form, such as graphene, h-BN, MoS_2, and MXenes, also have been explored and proven to be highly active for NO_xRR (Amrillah et al., 2021; Li et al., 2022; Liang et al., 2022b; Ouyang et al., 2022).

Although several limitations of metals in NO_xRR technology appear to hinder their utilization, the attempt to maximize the potential is growing. The downsizing of metals from nanoclusters into isolated single atoms could be one of the most effective schemes to maximize the active sites, thus increasing the catalytic performances (Cheng et al., 2019). This scheme, called single-atom catalysts (SACs), could reduce metal use. SACs are a class of catalysts in which the catalytically active individual and isolated metal atoms are anchored to support catalytic activity (Cheng et al., 2019). In SACs, all metal atoms are exposed to reactants and are available for more effective catalytic reactions (Cheng et al., 2019). Several SACs have been discovered, such as precious metal-based SACs (Pt, Au, and Ru) and non-precious metal-based SACs (Mo, Co, Ni, Fe, and Cr) (Zhai et al., 2020). Recently, SACs have attracted tremendous attention owing to their high metal utilization efficiency and excellent catalytic activity (Niu et al., 2021). SACs have been contributing as a connector between homogeneous and heterogeneous catalysts. Due to the high surface energy of single metal atoms, they are easy to aggregate into nanoclusters. It is important obtaining a proper choice of substrates to anchor the SACs into heterogeneous catalysts tightly [119]. Several reports of SACs in tandem with other catalytic materials are also available. For example, N-containing substrates have been suitable as tandem material with SACs, such as in C_3N_4, N-doped graphene (NG), N-doped carbon (NC), N-doped porous carbon (NPC), zeolitic imidazolate frameworks (ZIF) and metal oxide with defects (Zhai et al., 2020). Those materials have been discovered to stabilize SACs due to open porous structure, large surface area, abundant N species, and plentiful metal and oxygen vacancies (Zhai et al., 2020). These features could provide immense possibilities to anchor and stabilize SACs and enable mass transport during the electrochemical reaction (Zhai et al., 2020).

Heterogeneous catalysis could result in more efficient yields and allow facile isolation of NH_3 products compared to homogeneous catalysts (Abghoui et al., 2015). In fact, SACs are not the only ones that could be combined with other catalyst materials to boost the catalytic activity. In the nanocomposite form, combining catalytic materials in various forms was found to have more efficient catalytic activity than single catalytic material alone. The ultrafine Cu nanoparticles decorated porous TiO_2 (Chen et al., 2022) and Bi nanoparticles/carbon nanosheet composite (Q. Liu et al., 2022) are considered high-efficient catalysts for NO_xRR to NH_3. It was found that all the abovementioned examples have better catalytic activity than their pristine state. Combining two or more catalytic materials offers a broad development of catalysts for NO_xRR, and it may offer many new heterogeneous catalytic materials that will be discovered soon.

The development of catalyst materials for NO_xRR not only compels researchers to focus on the utilization of metal as the main ingredient but also non-metal catalytic materials. Though, as mentioned previously, 2D materials have been widely used for stabilizing the dispersed SACs, single 2D materials also offer excellent performance. 2D-based catalytic materials such as graphene, carbon, boron nitride (BN), boron carbide (B_4C), black phosphorus (BP), MXenes, and transition metal oxide/sulfide/nitride/phosphide have emerged as potential candidates for NO_xRR to NH_3 because of their distinctive physical, chemical, and electronic properties (G. Zhang et al., 2021). For electrocatalytic activity, the surface morphology, electronic structure, and effective active site were the main factors influencing the catalytic performance (X. Zhang et al., 2021). Specifically, the notable properties of 2D materials for electrocatalysts purposes are attributed because of some unique features and excellent chemical properties of 2D materials, being (i) ultrahigh specific surface area that promotes the adsorption of N_2 molecules, (ii) abundant defect sites of edge, and topological and vacancy defects that enable to serve as active sites, (iii) the electronic structures of 2D that can be precisely tailored *via* defect and surface engineering, as well as a heteroatom doping to improve the conductivity and generate new active sites, (iv) an atomic layered of 2D materials that could be advantageous to bridge the active sites and catalytic activities (G. Zhang et al., 2021). The properties of 2D materials potentially support the adsorption, activation, and electroreduction of N_2 molecules and the regulation of the active sites of N_2 and/or NO electroreduction at the atomic level (G. Zhang et al., 2021).

Natural 2D materials like graphene, TMD, MXenes, and unnatural 2D materials made from 3D materials were also reported to have the potential for NO_xRR. A NiO nanosheet array was

reported as a suitable electrocatalyst for high-performance NH_3 production through NO_xRR (Liu et al., 2021). Many more possibilities of those 2D material equivalents could be fabricated *via* thin-film deposition methods and other bottom-up layered solution syntheses, which then open a tremendous development of new electrocatalytic materials. Modifying the shape and morphology of nanomaterials would be beneficial to obtain high-efficient NO_xRR. In NO_xRR technology, a material with a large surface area is essential, and the surface area could be enlarged with modification of morphology. Not limited to 2D shape and form, other materials with one-dimensional (1D) forms are also suitable for NO_xRR. As reported, the FeP nanorod array (Liang et al., 2022b) and MnO_2 nanoarray with oxygen vacancies (Li et al., 2022) could serve as a high-efficient NO_xRR into NH_3 under ambient conditions. An amorphous boron carbide on TiO_2 in the form of nanobelt arrays also could be appropriate for obtaining high efficiency in NO_xRR to NH_3 (Liang et al., 2022a) and so as CoP nanowires on carbon cloth (H. Zhang et al., 2022).

Other than a modification in morphology and a proper combination of catalytic materials, development in the composition of catalytic materials by defect and vacancies also boosts electrocatalytic performances. Oxygen vacancy defects have a role in NO_xRR, e.g., the oxygen-defective MnO_2 nanoarray has been proven an efficient NO_xRR catalyst (Li et al., 2022). According to DFT calculations, the NO_x adsorption is enhanced on MnO_{2-x} (211) surface because of a strong electronic interaction between NO_x and Mn atoms for the presence of oxygen vacancies (Li et al., 2022). The beneficial defect is related to oxygen vacancy and other chalcogen vacancies, especially for TMD-based NO_xRR. Some studies have shown that sulfur vacancies in TMDs could activate N_2 and/or NO_x and enhance the electrocatalytic performance of TMDs (Tursun and Wu, 2021). The chalcogen vacancies could improve the electrocatalytic performance, such as scattered sulfur vacancies in MoS_2 can prevent the formation of NO dimers, and the vacancy sites exhibit improved catalytic activity than the pristine surface (Tursun and Wu, 2021). Zhang et al. reported enhancing NO_xRR to NH_3 by the CoS nanosheet with sulfur vacancies (L. Zhang et al., 2022).

With the tremendous need to overcome NO_x pollution, the development of electrocatalytic materials for NO_xRR is growing. The development of electrocatalytic materials involves downsizing, decorating, and compositing, all of which are interconnected, as shown in **Fig. 10**. Downsizing the scale of catalysts into an atomic regime is related to decreasing utilization needs of materials, such as noble metals and increasing the surface area interaction to improve the electrocatalytic activity. Decorating is also one of those ways to improve and modify the surface

area by making a suitable form and shape of electrocatalytic materials. Although 2D-shaped nanomaterials are more favorable for their large surface areas, some reports showed that material in 1D form is also suitable for NO_xRR (Ouyang et al., 2022). Compositing two or more electrocatalytic materials could also increase the electrocatalytic performances. One can combine the SACs with other electrocatalytic materials as a substrate. The combination of two or more electrocatalytic materials also could be done in several forms, such as in the nanoparticle's shapes, 2D-2D, hybrid 1D-2D, and/or 2D-3D shapes of nanomaterials. Lastly, the electrocatalytic materials for NO_xRR could also be improved by defect engineering, e.g., introducing the oxygen or chalcogen vacancies and compositing or element doping into the electrocatalytic materials to obtain a beneficial defect.

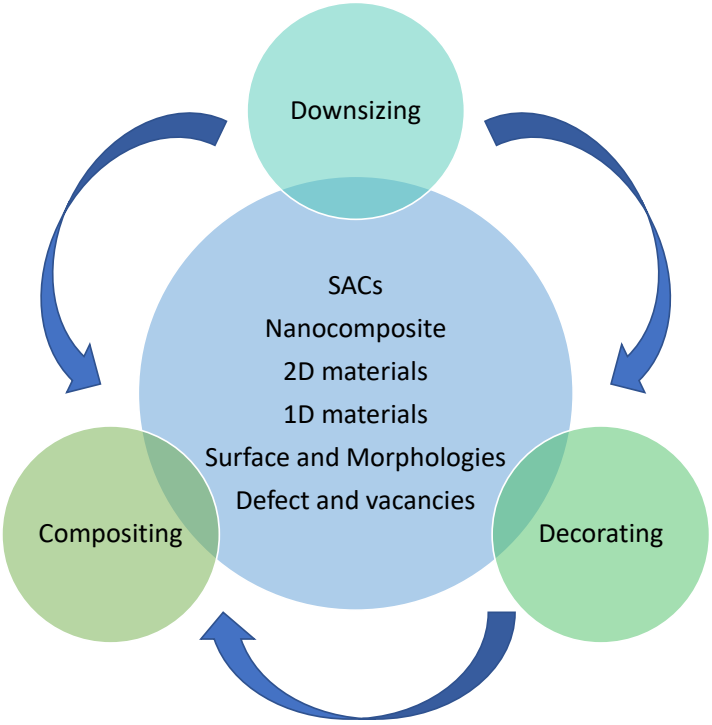

Fig. 10. Recent development of electrocatalytic materials in NO_xRR technology.

3.2 Reactor design for electrochemical NO_x conversion to NH_3

In addition to developing electrocatalytic materials, a NO_xRR reactor design is a key to obtaining a high-efficient electrocatalyst. Kim et al. proposed an electrode–electrolyte design-based NO_xRR as an alternative approach using a controlled amount of NO_x instead of N_2 (Kim et al., 2020). The design is illustrated in **Fig. 3**, where the NH_3 synthesis is conducted using the

NO_xRR process *via* electrolyte EDTA−Fe^{2+} metal complex (EFeMC) in combination with the nanostructured Ag cathode and its cycle (Kim et al., 2020). In this design, the gaseous NO_x was captured by an EFeMC-designed electrolyte containing 50 mM metal complex in a neutral-pH phosphate buffer solution (PBS), filled with a cathode chamber of an H-type electrolysis cell equipped with electrodes of working, counter (Pt foil), and reference (Ag/AgCl) (Kim et al., 2020). By this approach, the NH_3 production has a higher current density and a lower electricity price, further suggesting production cost could possibly reach the market price when the current density improved through some development of electricity (i.e., replacement with renewable electricity) (Kim et al., 2020).

The design of NO_xRR reactor or cells is essential to obtain highly efficient NO_xRR technology that is particularly relevant as the NO_xRR process's cost depends on the electricity utilization during the electrocatalytic process. Thus, renewable electricity prices could be a strategy to decrease the cost of production (Kim et al., 2020). Ko et al. proposed a design of a NO_xRR reactor, namely a gas-fed NO_x electrolyzer, in which NO_x emitted from mobile and stationary sources is then converted directly into N_2 or NH_3 *via* NO_x electrolyzer using batteries or renewable electricity. The produced N_2 can be emitted into the atmosphere, while NH_3 can be used as a crop fertilizer, as shown in **Fig. 11** (Ko et al., 2022).

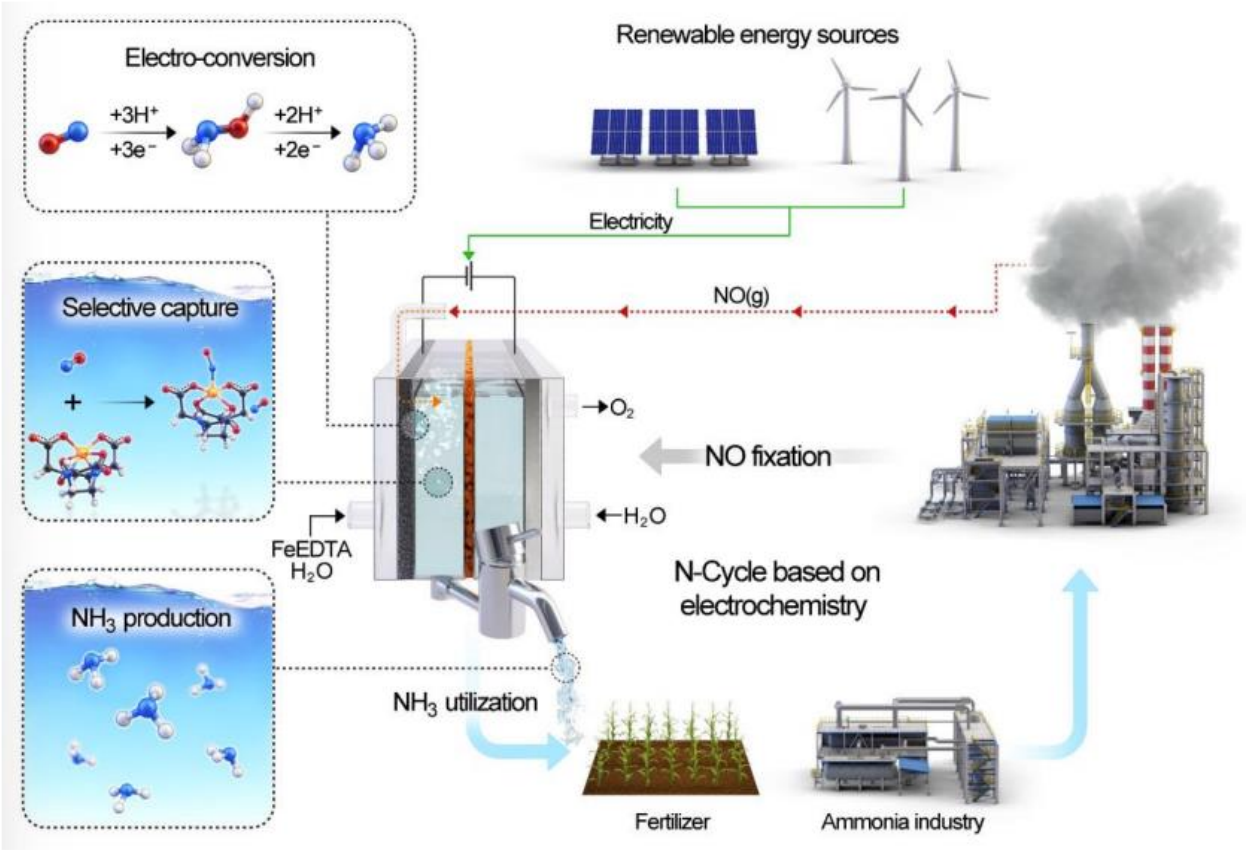

Fig. 11. The illustration of proof-of-concept-electrochemical NH_3 synthesis using NO_xRR in an electrolyte containing the EDTA−Fe^{2+} metal complex (EFeMC) integrated with a nanostructured Ag cathode and its cycle. Reprinted with permission from (Kim et al., 2020). Copyright 2020, American Chemical Society.

4. Perspective from life cycle and techno-economic analysis

Despite the encouraging results reported in recent investigations of waste streams to chemicals *via* sustainable electrochemical reduction overcoming technical challenges (Guo et al., 2022; Hao et al., 2022; Ma et al., 2021, 2020), those methods remain in the laboratory scales. Technology is thus inadequate to advance into large-scale deployment due to the high degree of complexity it may face in practical sites (Khoo et al., 2020). A more comprehensive evaluation of the overall process design is necessary to prevent the enormous potential of greenhouse gas emissions and undesirable process economics. The sustainability approach should be carefully assessed to ensure a favorable environmental profile, i.e., by a life cycle assessment (LCA) (Schoff, 2021). The cost-effectiveness viewpoint is imperative to identify a viable economic performance

by means of techno-economic assessment (TEA) (Kobos et al., 2020). LCA and TEA provide an encyclopedic evaluation of technologies, guide environmentally sustainable insights into research priorities, ensure the feasible production of value-added products to be marketed, and eventually accelerate the industrial adoption of air pollutants into chemicals *via* electrochemical reduction.

4.1 Life cycle assessment of CO_2 and NO_x electroreduction

Life cycle assessment, widely known as LCA, is a standardized tool to evaluate systems and/or processes throughout their life cycle (Cays, 2017; Muralikrishna and Manickam, 2017). By LCA, the studied systems or processes can evaluate their environmental friendliness from impact assessments following midpoint or endpoint indicators such as global warming potential, global energy requirement, acidic potential, etc. (Huijbregts et al., 2017; Matthews et al., 2014). LCA in the CO_2RR and NO_xRR is needed to give environmental guidance and identify critical steps in early-stage development, as most freedom degrees, or significant uncertainties commonly exist for emerging technologies. Although most technologies are still very young, applying LCA as early as possible in CO_2RR and NO_xRR is rather advisable in the process chain. The process of sustainable CO_2- and NO_x-based electroreduction requires significant energy input and are thus only logical to achieve a substantial reduction of CO_2 equivalent emissions if the energy consumed comes from renewable electricity sources. Most renewable electricity sources, such as solar photovoltaics, wind, hydro, biomass, etc., are proven to have far less greenhouse gas emissions than fossil fuel-based per energy output, of which emission is primarily embodied in infrastructures (e.g., up to 99% in photovoltaics) (UNECE, 2022). If the infrastructure is more durable than thought, influential impacts from greenhouse gas emissions may significantly decrease.

The environmental rationality behind the CO_2RR and NO_xRR prevails because renewable energy is readily available and thus can drive the operation of CO_2 and NO_x into valuable chemicals. As a reference metric, LCA can objectively identify the net difference between inputs and outputs of CO_2 equivalent emission in producing a mass unit of the electro-reduced valuable products as opposed to its relevant large-scale equivalents. As a result, an investigation of the larger-scale production of ethanol from CO_2RR presented reduced carbon footprints from solar- and wind-sourced electricity than from existing production of corn-sourced ethanol (Jouny et al.,

2018). Likewise, different scenarios for NO_xRR to NH_3 utilizing solar-sourced electricity gave lower environmental impact than considering the electricity mix, including fossil-based (Xue et al., 2021). By this finding, CO_2RR and NO_xRR will induce large-scale storage in chemical forms and on-demand conversion, which has the potential to solve the inflexibility problems posed by variable and intermittent renewable power generation that relies on seasonal and geographic constraints. In this sense, when there is excess electricity from solar photovoltaics or wind farms that otherwise would be curtailed, that electricity could be further used for CO_2RR and NO_xRR into a chemical (or fuel).

Table S2 presents the impact assessment of chemical products from CO_2RR and NO_xRR based on the LCA study. Per major chemical products of CO_2RR, LCA comparing net global warming impact and energy requirement of eight chemical products from one-step and two-step cycles CO_2RR, a study resulted in syngas $CO+H_2$ having lower environmental impacts, which later followed by methane, n-propanol, ethylene, formic acid, ethanol, acetic acid, and methanol (Kibria Nabil et al., 2021). Of all cases studied, two-step processes are found to be less emitted electrochemical conversion and less energy-consuming than one-step routes (Kibria Nabil et al., 2021). The electroreduction process enables avoiding a high-environmental impact process. For example, NO_xRR leads to the electrochemical recombination of nitrogen and water to form green ammonia by using the water hydrogen atoms directly without producing molecular hydrogen in the first place. In this way, producing hydrogen mainly pursued by fossil-fuel conversion can be avoided.

CO_2RR and NO_xRR to chemicals enable CO_2 emissions reduction if CO_2 and NO_x feedstocks are sourced from industrial waste, as most studies considered from flue gas of power plants, chemical facilities, or directly from the atmosphere (Barecka et al., 2021a; Jouny et al., 2018; Spurgeon and Kumar, 2018). Or instead of presuming a specific source, a study considered carbon footprint values of −0.5 and −0.8 kg CO_2-e per kg CO_2 feedstock as average assumptions (Kibria Nabil et al., 2021). In this way of utilization, if these products are even later burned and send CO_2 back to the atmosphere, it can potentially replace the corresponding production of typical petrochemical products. As long as the CO_2RR and NO_xRR products possess an overall better environmental profile, accordingly can be seen as a better environmental alternative, as it avoids an environmentally worse product than the commonly used case where CO_2 is simply emitted.

Waste to value-added products through the CO_2RR and NO_xRR processes does not compete with existing methods of manufacturing commodity chemicals as it serves as an addition to the established production process, meaning CO_2 and NO_x upcycling does not necessarily have a continuous operation and can be activated only upon the availability of renewable energy. For all the above reasons, the CO_2RR and NO_xRR will aid in decarbonizing the chemical industry, which is considered a hard-to-decarbonize sector.

4.2 Techno-economic assessment of CO_2 and NO_x electroreduction

Techno-economic assessment, or TEA, is a tool to analyze the economic performance of an industrial process, product, or service (Kobos et al., 2020; Murthy, 2022). The adoption of CO_2RR and NO_xRR to value-added products will require a multi-scale integration effort by connecting the advances from laboratory, plant, and supply chain scales; otherwise, these emerging technologies fail to transition from benchtop prototypes to industrial scale. To this extent, technical feasibility and profitability require a detailed analysis of capital, operating, revenue, and all associated costs of the developed systems by TEA, so that a deeper understanding of the economic balance for electroreduction systems will aid an optimized processes design at scale.

For any chance of commercialization, the primary limiting factor comes from a high capital expense of a critical component in the electroreduction process: electrolyzer units. Given that the currently available data of CO_2RR and NO_xRR electrolyzers are lacking, cost assumption in many studies is considered from water electrolyzers for hydrogen production as in many ways analogous and thus are expected to share many design features (Daiyan et al., 2021; Jouny et al., 2018). A study of techno-economic analysis for large-scale CO_2RR systems of various bulk chemicals reported that electrolyzers make up 20-45% of the total capital of base-case plants (Jouny et al., 2018), in some cases, even up to ~75% (Na et al., 2019). Given the current electrolyzer stack price, the capital expense can only be reduced by the cost reduction of the CO_2RR stack, which is likely to be higher for the early large-scale CO_2 electrolysis project and decline along with the growing market and by some characteristic amount each time accumulated experience. National Renewable Energy Laboratory (NREL) analyzed the scale effect of PEM electrolyzer production from 10 to 50000 units per annum, resulting in stack costs down by more than half price and leading to a very likely scenario for the future market (Mayyas et al., 2019).

Moreover, operation costs, primarily a function of electricity usage, contribute to the total operating expenses of as many as 30-85% (Jouny et al., 2018). Electricity, as a significant contributor to the operating costs, must be able to contribute to the prices of the chemical products from CO_2RR and NO_xRR at economic scales likewise or comparable to existing commercial prices (see **Table S2**). Employing renewable electricity is encouraging as it operates with low-carbon energy and is currently available at more attractive costs. As prices continue falling, renewables will become both carbon-neutral and low-cost energy sources that eventually drive viable electroreduction processes. Jouny et al. (Jouny et al., 2018) modeled different chemical products from CO_2RR for a production rate of 100 t a day for large commercial systems operating ~100 MW power (**Table S3**), suggesting a promising investment with payback times ranging from <1 to 9 years. The product prices are also in close agreement with the commercial markets. Upscaled production to 330 t a day (Adnan and Kibria, 2020) supported the prior finding, resulting in the same range of cost indicators normalized to the mass of produced chemicals. Increasing basis power utility to ~500 MW yielded significant cost indicators, thus raising the formic acid price to $1.16/kg (Spurgeon and Kumar, 2018) compared to $0.753/kg in the previous result (Jouny et al., 2018). As for NO_xRR, operation in 10 MW power, NO_xRR resulted in NH_4^+ (i.e., can be extracted to NH_3) levelized cost of <$3.4-3.8/kg according to different electricity sources, meaning to expect higher market price to make the positive margin per unit output and thus profitable (Daiyan et al., 2021). The presented capital and operating costs are re-estimated by noting the techno-economic parameters given in the study (Daiyan et al., 2021). Currently, the product price is not economic especially compared to the current commercial price of ammonia (**Table S3**), unless significant improvements are expected in close future.

Despite having issues that still need to be solved, the CO_2RR to formic acid/formate is currently one of the most promising industrial reactions (**Table S2**) and is thought to have the best chance on a practical scale. Recent gross-margin models developed to evaluate the techno-economic feasibility of producing different chemicals through CO_2RR also pointed out that formic acid is among the most economically viable products (Verma et al., 2016). According to global production, ethylene, methanol, ethanol, and carbon monoxide syngas are highly desirable major CO_2RR products due to a remarkably higher market capacity (Adegoke and Maxakato, 2022) (**Table S4**), as these four products provide versatile uses for energy generation, fuel additives, and chemical precursors. Noting NO_xRR, NH_3 has a large market capacity not only for global

agriculture and chemicals but also shed light on its advantages to the decarbonizing energy industry, thus giving producers and users versatility in its commercialization. The NO_xRR presents the feasibility of being an alternative renewable power-to-ammonia pathway for emerging hydrogen storage and can be transported over large distances using current infrastructure.

Cost optimization on CO_2RR and NO_xRR can be made by ensuring the propriety of performance indicators that influence the electrolyzer costs (e.g., current density, Faradaic efficiency, electrode configuration, etc.) to achieve significant improvements beyond the present performance. A report showed that higher electrolyzer stack costs could be balanced by operation under increased current densities (Barecka et al., 2021b; García de Arquer et al., 2020), thus leveraging cost. Increasing the current density to decrease the necessary electrolyzer area (as those parameters are inversely proportional) potentially lowers capital costs. Technology advances rapidly at very low-performance levels, but these effects will decrease after a certain degree of maturity, where energy efficiency and reliability barriers are traversed, and product markets are being chased (C. Chen et al., 2018). Hence, ensuring the local sensitivity and resetting the most critical factor in prior technical areas to determine which aspect should be improved at present (C. Chen et al., 2018; Na et al., 2019). Improvement of catalytic performance also highlights the importance of enhancing the yield of products. A study investigating the oxygen vacancy defect effect within CuO catalyst showed it has the highest yield for NH_4^+ (Daiyan et al., 2021). Subsequently, high yield coupled with the suitability of current density and cell potential will drastically reduce the cost of NH_4^+.

Coproduction of CO_2RR and/or NO_xRR with other chemical production can also allow cost reduction. For example, electrochemical processes coupling CO_2RR with organic oxidation reaction provided significant economic feasibility (Na et al., 2019). The integration of CO_2RR and less mature electrocatalytic in ethylene oxide manufacturing enables cost reduction and boosts CO_2RR profitability (Barecka et al., 2021b). This scheme has the potential to be adopted in other integrated electroreduction processes that employ synergies of waste streams and other process streams, which further creates an economic stimulus for the significant expansion of renewable energy in well-established bulk chemicals manufacturing while reducing the input of non-renewable feedstocks. A study also revealed that, apart from technology improvement, the economics of scale from combined CO_2 and NO_x capture systems have cut down the cost of NH_4^+

as NO_xRR products (Daiyan et al., 2021). CO_2 and NO_x capture processes are required to recover a high-purity product but remain uneconomical; thus, the exclusion of these capture technologies possibly lowers the capital costs by 20% to 60% (Daiyan et al., 2021). When capital costs are lower, yearly profits are of plausible value, and the system thus gives short payback time appealing for renewable energy investment. Payback times for industrial utilities range from 5 to 1 year for different CO_2 tax scenarios depending on the manufacture locality, scale, and electricity mix (Barecka et al., 2021b). **Table S4** shows various cost indicators of CO_2RR and NO_xRR products.

5. Conclusion and outlook

Direct use of CO_2 and NO_x gaseous pollutants from the atmosphere provides a new scenario for directly converting waste to chemicals. Nonetheless, capturing and concentrating CO_2 and NO_x from polluted air requires advanced facilities that may limit the practical relevance of this concept. Moreover, the low solubility of CO_2 and NO_x gas in aqueous electrolytes restricts mass transport and becomes an unfavorable environment for the CO_2RR and NO_xRR. These problems remain grand challenges associated with the CO_2RR and NO_xRR that recently gathered significant interest.

There are numerous methods of treating CO_2 and NO_x pollution, some of which have been industrially implemented, and others are being developed to overcome the limitations of traditional treatment techniques. The CO_2RR and NO_xRR arise as promising and effective technologies due to their ability to drive the conversion of CO_2 and NO_x gases into various hydrocarbons chemical and NH_3, respectively, which support the waste-to-chemicals conceptualization. The CO_2RR and NO_xRR have some aspects in common. Both pathways frequently utilize noble metals such as platinum (Pt) and palladium (Pd) to assist the electrocatalytic reduction processes. Various strategies are, however, necessary to overcome the cost-inefficiency of those noble metals. Similar approaches have been conducted in the CO_2RR and NO_xRR by using low-cost elements, e. g., transition metal (Cu, Ti, Ni) and two-dimensional materials (graphene, h-BN, MoS_2, MXenes). Since the high surface reaction is vital in the CO_2RR and NO_xRR, strategies to enhance the surface interaction of the electrocatalyst materials are thus carried out to aim for increased efficiency, including compositing, morphology and shape modification, and doping of the electrocatalytic materials. The electrolyte also holds a vital role in the CO_2RR and NO_xRR, so the two pathways require similar strategies for appropriately choosing electrolytes that excellently support the

electrocatalytic reduction process, exhibit excellent solubility with CO_2 and NO_x, have good ionic conductivity and wide potential window. The low solubility of CO_2 and NO_x in some aqueous electrolytes hinders the development of electrocatalytic reactors having mass transport. Their solubility problem becomes an unfavorable environment for the CO_2RR and NO_xRR. These problems are among the remaining significant challenges in the CO_2RR and NO_xRR to solve.

Developing a versatile and straightforward fabrication of single-atom catalysts (SACs) is significant for furthering their application in CO_2RR and NO_xRR technologies. Physical and chemical synthesis techniques to fabricate SACs are done by varying the interaction between the metal centers and the coordination defects of the supports so that accurate control over their local structure and the increment of the active-site density could be achieved. A rational design of the atomic structure of SACs is decisive for its intrinsic activity that further influences its adsorption and activation performance over single sites. The effect of metal loading of SACs also affects the density of active sites and, thus, further mass activity. Extensive discovery of nanomaterial fabrication techniques would ease the development of catalytic materials for CO_2RR and NO_xRR technology. For SACs, top-down synthesis methods would be more suitable and easier since very small up to atomic sizes of materials could be achieved. Bottom-up synthesis is ideal for constructing the desired nanomaterials for catalytic materials in the form of nanocomposites and different shapes of nanomaterials (2D and 1D). Chemical, physical, and biological synthesis approaches could be suited to obtain catalytic materials. The chemical synthesis approach may be more favorable and could be developed easily; physical methods would also be important in developing catalytic materials with higher throughput; while the biological synthesis approach would be a saver and eco-friendly.

Searching for novel electrocatalysts *via* high-throughput screening can be further attempted. Inputting catalyst candidates' physical, electrical, and chemical properties in high-throughput screening allows it to screen out the best catalytic materials for the CO_2RR and NO_xRR from hundreds of possibilities. It is noted that the CO_2RR and NO_xRR in aqueous systems exhibit more complex and dynamic reactions under different electrolytes (salts and concentrations). Moreover, some electrolytes behave as gas capturers to increase the solubility of CO_2 and NO_x gases, resulting in a high conversion yield. Computational simulations in such dynamic molecular levels will provide unexpected insights into the underlying mechanisms behind CO_2RR and NO_xRR in an

aqueous solution and reveal which pathway may take place, as has been exemplified in many works of literature, including that with molecular catalysts such as copper(II)-porphyrin complex (Y. Zhang et al., 2022b).

Cell configurations and reactor design optimization for capturing and converting air pollution are exciting fields to explore. While there are many interesting electrocatalyst developments, only a few research covers this field. The 3-electrochemical or H-type cell is generally used in lab bench experiments, and optimization of the electrochemical reactor is a critical aspect of large-scale applications. To date, some reactors are being developed, being membrane electrode assembly (MEA) electrolyzers, microfluidic reactors (MFR) assembled with gas diffusion electrodes (GDE), membrane-based flow reactors (MR), etc., to meet the industrial requirement. It is believed that, aside from electrocatalytic properties, reactor designs significantly impact reaction rate, selectivity, and stability.

Serving CO_2 and NO_x as resources rather than waste *via* CO_2RR and NO_xRR will present advantages over typical chemical production processes only if coupled with renewable electricity sources. Otherwise, the realization will only be utopian if the electricity still relies on fossil-based sources, as the CO_2RR and NO_xRR obviously cannot offer better environmental profiles. The CO_2RR and NO_xRR using renewables will benefit from lowering environmental impacts, enabling large-scale storage in chemical forms, and decarbonizing the chemical industry. The cost-effectiveness of CO_2RR and NO_xRR is crucial to realize the technology. Given the high capital expense, it is challenging to afford the product prices competing with the current commercial prices. Therefore, efforts should be strived to achieve significant improvements in fundamental parameters of electrochemical conversion and cost reduction of components associated with CO_2RR and NO_xRR unless the product price will never satisfy an economical scale. To that extent, it is also noted to ensure that operating costs from renewable electricity constantly decline. Additionally, integrating CO_2RR or NO_xRR with other production streams may reduce costs. With the growing market and accumulated experience in the foreseeable future, the technology costs are hoped to be lower than the current ones.

Even though fossil-fuel-based chemicals are still the most economic at present, the concern of greenhouse gas will trigger the use of carbon capture storage technology, eventually increasing its price. In the future, fossil fuel is expected to be scarce, so its costs will also increase. The

development of CO_2RR and NO_xRR may achieve a commercially viable production plant with urgent improvement to be called for. Further major investigations on CO_2RR and NO_xRR will be necessary to validate our assumption on transforming waste into valuable chemicals toward a sustainable production powered by green energy.

Author contribution

A.H. : Conceptualization, Methodology, Visualization, Writing - Original Draft, Writing - Review & Editing, Funding Acquisition; **T.A.** : Writing - Original Draft, Investigation, Funding acquisition; **V.N.A**. : Writing - Review & Editing, Funding Acquisition; **J.R.** : Supervision; **Z.W.S**. : Writing - Review & Editing, Funding Acquisition; **N.T.** : Supervision. **A.H.** is the main contributor to this manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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