CO_2 Conversion in Water Microdroplets

*Yugen Zhang**

Yugen Zhang
Institute of Sustainability for Chemicals, Energy and Environment (ISCE2), Agency for Science, Technology and Research (A*STAR), 1 Pesek Road Jurong Island, Singapore 627833, Republic of Singapore.
E-mail: zhang_yugen@isce2.a-star.edu.sg

Keywords: water microdroplet, CO_2 conversion, reaction acceleration, enabling

Abstract: Microdroplet chemistry is gaining recognition as a powerful tool and promising platform due to its unique physicochemical environment, suitable for a wide range of applications. When scaled down to the nano- or micrometer range, microdroplets possess a high surface-to-volume ratio and exhibit several distinctive properties, such as strong interfacial effects, electric fields, super acidic or basic environments, radical generation, and enhanced reducing power. These characteristics contribute to accelerated reaction rates and enable reactions that are otherwise unfavorable. This minireview explores and discusses the applications of microdroplet chemistry in CO_2 conversion processes. abstract text here.

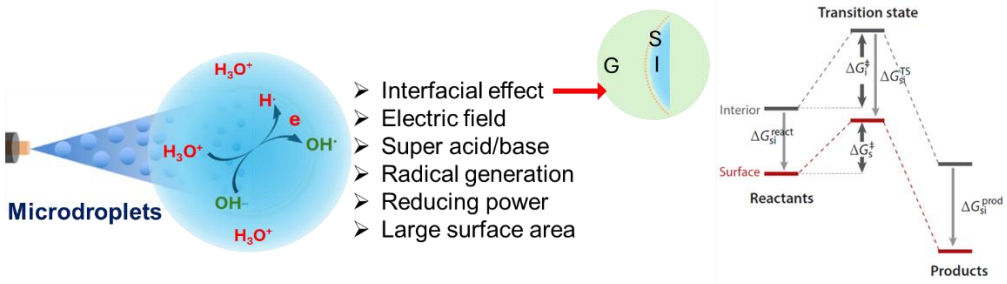
1. Introduction

Microdroplet chemistry is a burgeoning field that explores the unique chemical reactions and processes occurring within micro-scale droplets.[1-3] This area of study has significant implications for various scientific disciplines, including organic synthesis, analytical chemistry, environmental science, materials science, and biomedical applications.[1,4,5] For example, recent studies have discovered that charged microdroplets can spontaneously form nanoparticles from natural minerals.[6] This phenomenon demonstrates how powerful tool of microdroplet and indicates significant implications for environmental and materials science, as it suggests a new method for synthesizing nanomaterials without the need for external reagents or complex procedures. While one of the most remarkable features of microdroplet chemistry is the acceleration of reaction rates and occurrence of unfavorable reactions.[1,7,8] Studies have shown that chemical reactions can occur up to a million times faster in microdroplets than in bulk solutions. This phenomenon is attributed to several factors, including increased surface area-

to-volume ratio, rapid mixing, and the presence of unique interfacial effects and unusual physicochemical environment. With sustainability and carbon emissions becoming urgent global concerns,[9] the innovative field of microdroplet chemistry has shown significant potential in CO_2 conversion, contributing to global carbon mitigation efforts. In this review, we will summarize the applications of microdroplets in CO_2 conversion, with a particular focus on the unique aspects of microdroplet chemistry and a discussion of its underlying mechanisms.

2. General mechanism of microdroplet chemistry

Microdroplets are typically generated through techniques such as electrospray ionization (ESI), gas spray, micro-printing, or ultrasonic atomization. These methods produce droplets ranging from nanometers to micrometers in diameter. Microdroplet chemistry involves performing chemical reactions within these tiny droplets, where solvents and reagents are dispersed, creating highly confined and reactive environments, scheme 1.



Scheme 1. Water microdroplet and its unique properties. Charge separation and radical generation are general phenomena of water microdroplets.[10, 11] Microdroplet interface is partial solvation and the reaction on interface has smaller energic barriers.[1,11]

The accelerated reaction rates observed in microdroplets are still under investigation, but several hypotheses have been proposed:[1, 7,8,10-17]

Interfacial Effects: Microdroplets exhibit several unique characteristics, such as high surface area, surface tension, partial solvation at the surface, ordered molecular orientation, reagent confinement, and pH alteration. These features create an extensive interfacial region where distinct catalytic and reactive species can form, significantly enhancing reaction rates.

Concentration effects: Solutes within microdroplets can become highly concentrated at the interface, leading to increased local reactant concentrations and, consequently, faster reaction kinetics.

Microenvironment: The confined space within microdroplets can modify the physical and chemical properties of reactants, promoting more rapid reactions. For instance, within water

microdroplets, super acids, bases, electrons, radicals, and oxidants can spontaneously generate, facilitating swift chemical reactions.

Electric fields: The electric field at the surface of the aqueous microdroplet was found to be on the order of 109 V/m.[18] The electric fields present within microdroplets can alter reaction mechanisms, often leading to the formation of products that are not typically observed in bulk-phase reactions. The charge on microdroplets can also significantly impact the thermodynamics of redox reactions, resulting in faster reaction rates compared to bulk solutions.

Different setups and conditions—such as charged versus non-charged sprays, catalytic versus non-catalytic systems, and the use of various substrates—can introduce unique reaction mechanisms specific to each system. These variations can greatly influence the outcomes and efficiency of the reactions, leading to distinct behaviors and products depending on the specific configuration and environment.

Multiple factors influence CO_2 conversion reactions in microdroplets, with both enthalpic and entropic effects playing fundamental roles.[19] In the condensed phase, desolvation presents a significant energy barrier for reactants to reach the transition state. The enthalpic effect of partial solvation can lead to a 2–20 kcal/mol difference in activation energy between gas-phase and solution-phase reactions, contributing to the observed orders-of-magnitude increase in reaction rates. Additionally, entropic effects arising from the ordered arrangement of solvent and reactant molecules may result in a reduction of approximately −2.3 kcal/mol in activation energy and −2.0 kcal/mol in Gibbs free energy. These combined effects enhance the reaction efficiency within microdroplets.

3. CO_2 reduction in water microdroplet

The rising concentration of carbon dioxide (CO_2) in the atmosphere is a critical environmental challenge, necessitating innovative strategies for mitigation.[20-22] One promising approach is the conversion of CO_2 into valuable chemicals and fuels, though this remains particularly challenging due to the inherent stability of CO_2.[23-25] Recently, the use of water microdroplets has emerged as an innovative and efficient platform for CO_2 reduction.[26] Microdroplets offer a unique reaction environment that can significantly enhance reaction rates and modify reaction pathways. Their high surface area-to-volume ratio, coupled with distinctive interfacial properties, creates a confined space where CO_2 can be captured and reduced more effectively.

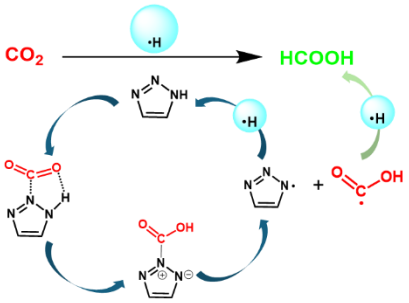
Table 1. A summary of parameters and conditions of CO_2 conversions in microdroplets.

Nebulization method	Droplet size μm	Catalyst	Co-solvent	Products	Measurement	Bulk phase reaction	ref
Spray nebulizer (CO_2)	10	1H-Tz	none	HCOOH (71 μM)	MS	No reaction	28
Nanoelectrospray Ionization (nanoESI, 4kV)	10-15 (nozzle)	Cu(phen)	none	HCOOH (1100 μmol/L)	MS	No reaction	33
Electrospray (- 6 kV)	50-100 (nozzle)	$Cu(phen)_2$ $KHCO_3$	none	HCOOH, CH_3COOH, CH_3CH_2OH, CH_3OH (80 μM)	MS / NMR	No reaction	34
Piezoelectric nozzle (print)	200	WO_3/UV	none	HCOOH (2536 $\mu molh^{-1}\ g^{-1}$)	GC	13 $\mu molh^{-1}\ g^{-1}$	36
Spray nebulizer (CO_2)	100 (nozzle)	none	none	HCOO- (70 μM) CH_3COO- (19 μM) $HOCH_2CH_2OH$ (48 μM) CH_4 (4.6 μM)	NMR	No reaction	39
Electrospray (- 4 kV)	70 (nozzle)	None	acetone	Phenylacetic Acid (yield 3.2%)	MS	No reaction	41
Spray nebulizer	100 (nozzle)	none	none	Pentafluorobenzoate (conversion 71%)	MS	No reaction	43
Electrospray (- 4 kV)	100 (nozzle)	$(NH_4)_2CO_3$	none	β-diketo acid (conversion 70%)	MS	No reaction	44
Nanoelectrospray Ionization / Electrospray	5 / 250 (nozzle)	none	ACN	Carbamic acid (conversion 60%)	MS	Yield 14%	48
Nanoelectrospray Ionization 1.6 kV	10 (nozzle)	NH_4HCO_3	none	Carbamic acid (conversion 93.7%)	MS	NA	49
Electrospray (40 V)	6-12.5	$CuBi_2O_4$	none	Urea (12.3 mmol $h^{-1}\ g^{-1}$)	MS / HPLC	3.36 mmol $h^{-1}\ g^{-1}$	52
Spray nebulizer	90-100	$[C_1C_2Im]I$/ PhOH	none	Epichlorohydrin carbonate (yield 85%)	NMR	Yield < 5%	55
Electrostatic atomizers	10-30	[HMIM]I	ACN	Epichlorohydrin carbonate (yield 96%)	GC	Yield < 5%	56
Ultrasonic nebulizer	NA	TEG/KI	CH_3OH	Styrene carbonate (yield 78%)	NMR	Yield 30%	57

3.1 Triazole catalyzed CO_2 to formic acid in water microdroplet

The transformation of carbon dioxide (CO_2) into formic acid (HCOOH) is a highly sought-after reaction, as formic acid offers a practical solution for hydrogen storage and serves as a key feedstock for fuels and chemicals.[27] Traditionally, formic acid is synthesized from CO_2 and reductants using metal catalysts, electrochemical methods, or photochemistry. However, in 2022, Zare and colleagues reported an exciting method for the direct production of formic acid from CO_2 gas by utilizing room-temperature water microdroplets containing dissolved 1,2,3-triazole (Tz) as a catalyst.[28] In their study, a maximum conversion yield of captured CO_2 exceeding 80% was achieved, with a formic acid concentration of approximately 71 μM within

the microdroplets. This process leverages the significantly larger gas−liquid contact surface area provided by water microdroplets, which enhances CO_2 capture and reduction. The findings reveal that Tz in sprayed water microdroplets can effectively capture gas-phase CO_2 and convert it into formic acid with remarkable efficiency. The ultrafast conversion and high yield suggest that Tz/water microdroplets could act as effective CO_2 scavengers, presenting a novel and promising approach for formic acid production.



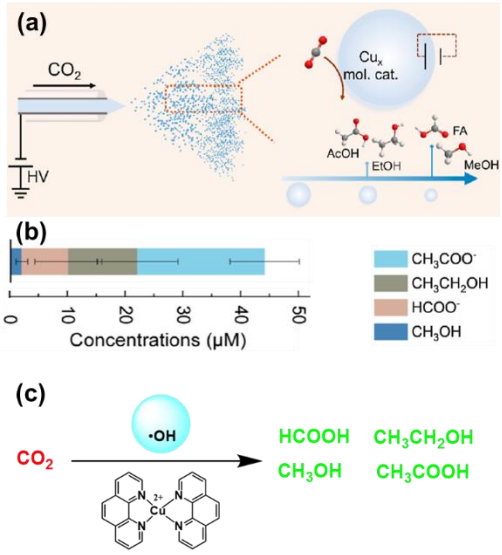
Scheme 2. Triazole catalyzed CO_2 reduction in water microdroplet. [29]

Subsequently, a molecular level reaction mechanism was elucidated by using quantum chemistry calculations and ab initio molecular dynamics (AIMD) simulations.[29] One possible multistep mechanism was presented which including: (1) the adsorption of CO_2 by 1,2,3-triazole (Tz) to form a CO_2-Tz complex; (2) the complex undergoes intramolecular proton transfer from Tz to form COOH-Tz^-; (3) the complex undergoes reduction, and the C−N bond dissociates to produce •COOH which captures a •H radical from water microdroplet interface to form HCOOH, Scheme 2. AIMD simulations highlight the critical role of water and the air-water interface in generating radicals and electrons. These simulations also offer valuable insights into the mechanistic, kinetic, and dynamic processes involved in converting gas-phase CO_2 into valuable products using azoles or amines dissolved in water microdroplets.

3.2 Copper complex catalyzed CO_2 reduction

Microdroplet systems have been demonstrated as a powerful tool to accelerate various reactions. It was investigated that within water microdroplets, electrons can be spontaneously generated as OH^- ions, then transform into •OH radicals,[30-32] which can capture and reduce CO_2. In one study, microdroplets generated by directly spraying water solution with Cu catalyst into the air can significantly enhance CO_2 to formate conversion.[33] The reaction consequence is proposed as: H_2O autoionizes into H^+ and OH^- ions; subsequently, the OH^- ions donate an electron, transforming into •OH radicals. This enables CO_2 to be captured and spontaneously

hydrogenated into HCO_2^-. This process may be driven by a strong electric field at or near the microdroplet interfaces. The presence of $phenCu^{2+}$ (phen, 1,10-phenanthroline) and the introduction of additional CO_2 as a reactant resulted in a significant increase in formic acid production, up to 4000 times higher. Within microdroplets, Cu ions undergo valence alternation, facilitating the deposition of electrons and the promotion of formate conversion. This work demonstrated that under ambient conditions and without any additives, water microdroplets can capture CO_2 and reduce it to formate.

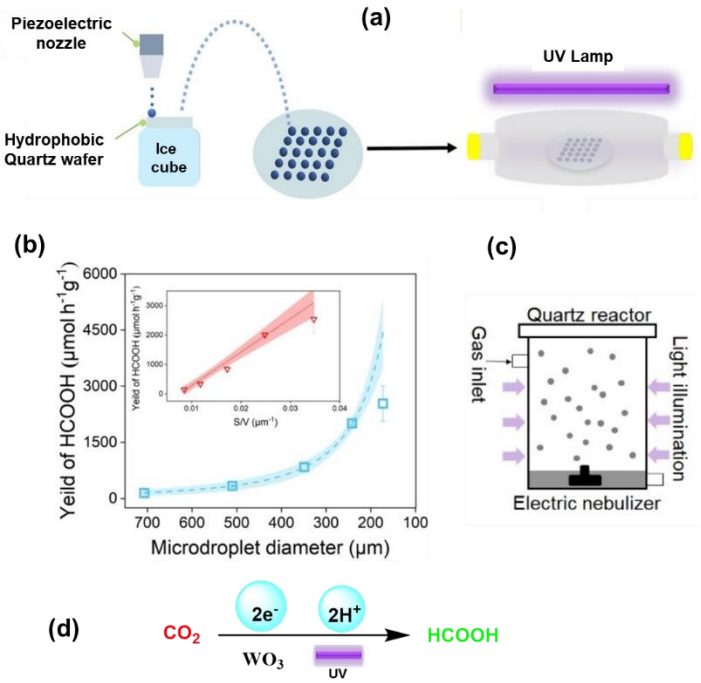


Scheme 3. (a) Schematic illustration of Cu-catalyzed CO_2 reduction and C-C coupling in electrospray-generated water microdroplets. (b) Product concentrations under -6 kV, 0.1M $KHCO_3$, 20 mM catalyst concentration and gas flow rate 600 SCCM. (c) Scheme of the reactions. Modified from ref. 34 with permission from John Wiley and Sons, copyright 2023.

More recently, Fan et al reported that charged microdroplets generated by electrospray can effectively serve as microelectrochemical cells (MECs) for CO_2 reduction and C−C coupling, scheme 3.[34] In this system, $CuII(phen)_2$ catalysts are applied and undergo reconstruction during the reaction, forming various Cu status (Cu(I), Cu(II) and Cu(III)) which are crucial for catalyzing C−C coupling to produce ethanol and ethyl acetate. Unlike previous reports of one-electron reaction processes in microdroplets, it was observed the multielectron/proton transfer to generate C_2 products in the CO_2 reduction reaction (CO_2RR) for the first time. Although the yields achieved in this study are not yet optimal and the detailed reaction pathway is not clear, results reported in this study hold promise for enabling more complex and efficient electrochemical reactions in future research.

3.3 Photocatalytic CO_2 reduction at microdroplet

The solar-driven CO_2 reduction reaction (CO_2RR) is often hindered by slow mass transfer and the rapid recombination of photogenerated charge carriers.[35] Recently, it was reported that the photocatalytic CO_2RR efficiency at the abundant gas-liquid interface of microdroplets is two orders of magnitude higher than in the corresponding bulk phase reaction, even without the use of sacrificial agents.[36] It is reported that the production rate of formic acid over $WO_3 \cdot 0.33H_2O$ facilitated by microdroplets reaches 2536 μmol/h·g, compared to just 13 μmol/h·g in the bulk phase. In contract to typical spray-flying microdroplets, this enhancement was demonstrated on a static microdroplet on a superhydrophobic quartz substrate, generated using a multi-pass printing mode with a microdroplet printer, scheme 4. The photocatalytic CO_2RR performed in the microdroplet under a 365 nm UV lamp, and the resulting products were monitored using ion chromatography (IC) and gas chromatography (GC). The yields of HCOOH produced using $WO_3 \cdot 0.33H_2O$, Au/TiO_2, and Au/ZnO in microdroplets reached 2536.23, 1843.45, and 1891.80 μmol/h, respectively, which are over two orders of magnitude higher than those observed in the corresponding bulk reactions (13.32, 5.41, and 7.42 μmol/h). Interestingly, methanol was also observed in the system as a side product and its yields in the microdroplet reaction system reached 789.01, 1562.51, and 1437.45 μmol/h for the respective catalysts, significantly surpassing the yields in bulk reactions.

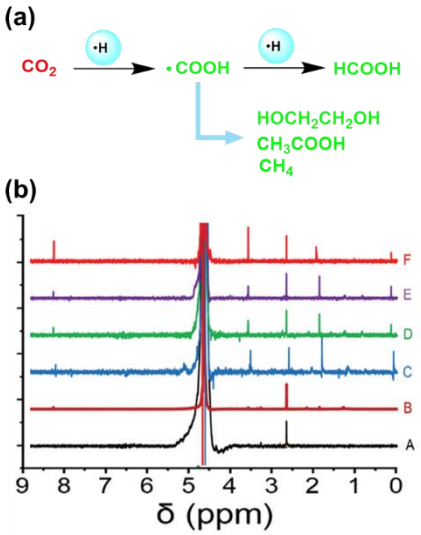


Scheme 4. (a) A setup featuring photocatalytic static microdroplets on a superhydrophobic quartz substrate, generated using a microdroplet printer. (b) Formic acid yields increase significantly as the size of the microdroplets decreases. (c) A circulating photocatalytic microdroplet system designed for scaling up experimental processes. (d) Reaction equation. Modified from ref. 36 with permission from John Wiley and Sons, copyright 2024.

This performance marks a substantial improvement over previously reported photocatalytic CO_2RR under bulk phase reaction conditions.[37] The redox potential at the air-water interface has been found to differ significantly from that in the bulk phase. Recent research indicates that on the surface of air bubbles in water, the oxidation potential of OH^- to •OH is at least 0.7 V lower than the values listed in redox tables.[38] This phenomenon is attributed to the electrostatic destabilization of the hydroxide anion in water, which accelerates the generation of electrons and hydroxyl radicals at the air-water interface. Therefore, the enhanced photocatalytic CO_2RR performance in microdroplets is closely linked to the interfacial electric fields within the droplets, which promote the separation of electrons and holes, along with the efficient delivery of CO_2 to photocatalyst surfaces within microdroplets. Furthermore, increasing CO_2 solubility in the microdroplet solution could further improve photocatalytic performance. The feasibility of scaling up photocatalytic CO_2RR in microdroplets was validated using a circulating electric nebulizer in a large quartz reactor, achieving a scaled-up photocatalytic CO_2RR rate of 71.39 μmol/h. This study introduces a novel approach to overcoming the low efficiency of photocatalytic CO_2 reduction to fuels, which has the potential for scalability.

3.4 Catalyst-free CO_2 hydrogenation

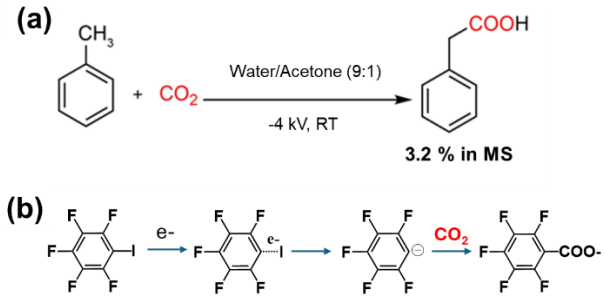
Water microdroplets exhibit strong reducing power, and studies have shown that CO_2 can be directly reduced within these droplets without the need for a catalyst or reducing agent. Zare's research team developed a carefully designed direct nebulized spray system, demonstrating that CO_2 could be converted into small molecules such as formate anion ($HCOO^-$), acetate anion (CH_3COO^-), ethylene glycol ($HOCH_2CH_2OH$), and methane (CH_4).[39] The concentration of the products in the droplets varied depending on the nebulization gas used, as illustrated in Scheme 5. In a pure CO_2 atmosphere, higher amounts of formate anion were produced, with a concentration of approximately 70 mM, as confirmed through NMR analysis. This result highlights the unique role of water microdroplets in CO_2 transformation processes.



Scheme 5. (a) CO_2 converted to formic acid, acetic acid, ethylene glycol, and methane (CH_4) in microdroplet. (b) Water-suppressed NMR of unsprayed control under nitrogen atmosphere A), removed CO_2 water by purging nitrogen and sprayed by nitrogen B), water microdroplets sprayed by nitrogen C), oxygen D), compressed air E) and carbon dioxide F) sheath gases.

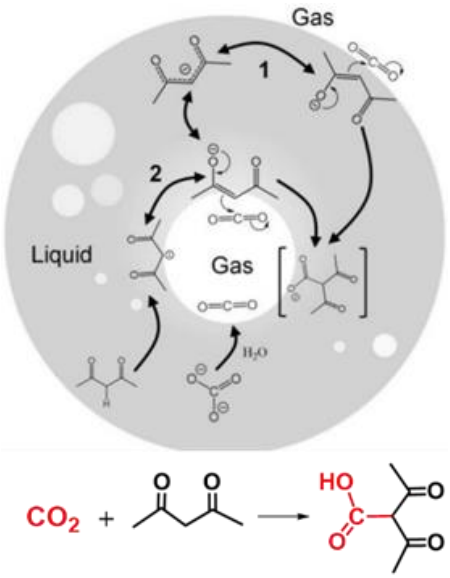
4. Direct carboxylation with CO_2 in microdroplet

Direct C-H activation and coupling with CO_2 is one of the most sought-after reactions for converting CO_2 into valuable chemicals and fuels. Traditionally, this reaction demands specialized catalysts, as well as high temperature and pressure conditions.[40] However, recent studies have shown that C-C (C-H/CO_2) coupling can occur under very mild conditions within an electrospray ionization (ESI) microdroplet environment. Negatively charged water microdroplet facilitates the generation of hydroxyl radicals at the water-gas interface, which initiates the formation of organic radicals and coupling with CO_2. Zare's team demonstrated that toluene could react with carbon dioxide in the presence of a negative voltage applied at the sprayer source, leading to the formation of phenylacetic acid without the need for catalysts or toxic reagents.[41] This study presents a groundbreaking one-step method for synthesizing phenylacetic acid and its derivatives using water microdroplets at room temperature without the need for metal catalysts or toxic reagents, significantly simplifying the synthesis process, scheme 6a. This reaction is proposed undergoing radical-mechanism by the formation of benzyl radicals and subsequently reacting with carbon dioxide to produce phenylacetic acid. The method allows for the rapid generation of important pharmaceuticals, including 4-aminophenylacetic acid and 3,4-dihydroxyphenylacetic acid, enhances the efficiency of drug synthesis and promotes eco-friendly practices in pharmaceutical manufacturing.[42] However, its potential industrial applications depending on the operation scale, efficiency and cost.



Scheme 6. Microdroplet facilities direct carboxylation toluene (a) and iodopentafluorobenzene (b) with CO_2.

The redox potential at the air-water interface in microdroplet could accelerates the generation of electrons and hydroxyl radicals. Recently, Zhang et al reported using reducing power of water microdroplets to generate an unusual radical anion of iodopentafluorobenzene ($C_6F_5I^{\bullet-}$) by simply spraying (non-charged) a water solution of C_6F_5I into microdroplets in a nitrogen-filled glovebox, realized a direct carboxylation of phenyl ring under very mild conditions, scheme 6b.[43] Water microdroplets generate electrons to reduce C_6F_5I to $C_6F_5I^{\bullet-}$, with the excess electron facilitating the C−I bond breaking and the formation of the $C_6F_5^-$ anion, which subsequently fixates CO_2 into $C_6F_5CO_2^-$. This study demonstrates a novel example of CO_2 utilization and introduces a catalyst-free strategy that leverages the reducing power of water microdroplets, although it is exampled on a special electron-rich aromatic substrate. This approach holds potential for a wide range of reactions, such as reductive coupling and hydrogenation with charged or non-charged water microdroplets.

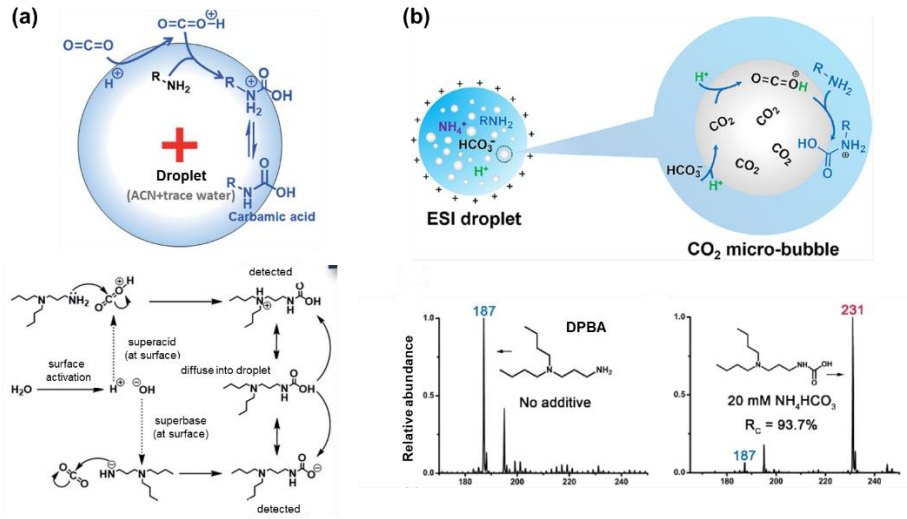


Scheme 7. The ketone-CO_2 coupling pathway under water microdroplet with CO_2 bubbles. Reproduced from ref. 44 with permission from John Wiley and Sons, copyright 2024.

In another study, it was reported a catalyst-free method for the coupling carbon dioxide with α-carbon of ketones to form carbon-carbon bond, at the air-water interface of negatively charged aqueous microdroplets (ESI) under ambient conditions.[44] The reactions occur through the generation of a carbanion at the α-carbon of a ketone, which then undergoes nucleophilic addition to CO_2, scheme 7.[45] The kinetics of the reaction are influenced by factors such as reagent concentration, CO_2 gas pressure, and the distance travelled by the droplets. At low ketone concentration, high conversion rate was achieved as most of the AcAc anions are available at the surface to participate in reaction with CO_2.[46] The spray potential has a minimal effect on the conversion ratio. Interestingly, when $(NH_4)_2CO_3$ was used as additive in this reaction, the conversion rate rises quickly from 10 to 70% by increasing the $(NH_4)_2CO_3$ ratio from 5 to 30%. This result shows again that $(NH_4)_2CO_3$ could be used as internal CO_2 source to promote the reaction. Other factors include water/methanol ratio and flying distance, salt additives have also been studied. Theoretical calculations indicate that water within the microdroplets plays a key role in enabling this unique chemistry. The reaction is not supported by organic solvents. Water in the droplet helps in holding the net charges due to its high dielectric constant and drives the generation of the carbanion to react with CO_2 at the interface. In addition, the equilibrium of ammonium carbonate to CO_2 conversion will also benefit from water which helps in generating microbubbles for the reaction to occur. These findings again demonstrate a green pathway for converting CO_2 into valuable carboxylate organic products.

5. Carbon-nitrogen bond formation with CO_2 in microdroplet

The reactions between amines and carbon dioxide (CO_2) are mild, reversible, and among the most commonly used carbon fixation processes today, including in industrial CO_2 scrubbing systems.[47] Recently, it has been reported that carbamic acid can form through the reaction of amines with CO_2 in electrospray ionization (ESSI) microdroplets, scheme 8.[48] The reaction is sensitive toward amines and CO_2 concentration. Using carbon dioxide-assisted electrospray ionization (ESSI), which is significantly more efficient than N_2-assisted ESSI, the formation of carbamic acid was observed for various primary and secondary amines diluted in acetonitrile/water. This method achieved up to 60% amine conversion. No products were observed for the aromatic amines. It was observed that adding trace amounts of water to an organic solvent significantly increased carbamic acid production, suggesting that the enhancement is due to the superacid/superbase properties of an aqueous surface, which can activate the functional groups involved in the reaction. The superacid protonates CO_2, making it more electrophilic, while the superbase deprotonates the amine, increasing its reactivity. This interfacial chemistry is responsible for the observed increase in carbamic acid formation, rather than reactions involving dissolved CO_2 in the form of bicarbonate. The presence of large amounts of water, however, inhibits the reaction. Although this is a small-scale reaction and the products were only observed in Mass spectroscopy, the finding suggests that microdroplet reactions could be an effective method for screening reagents for carbon dioxide capture and storage.

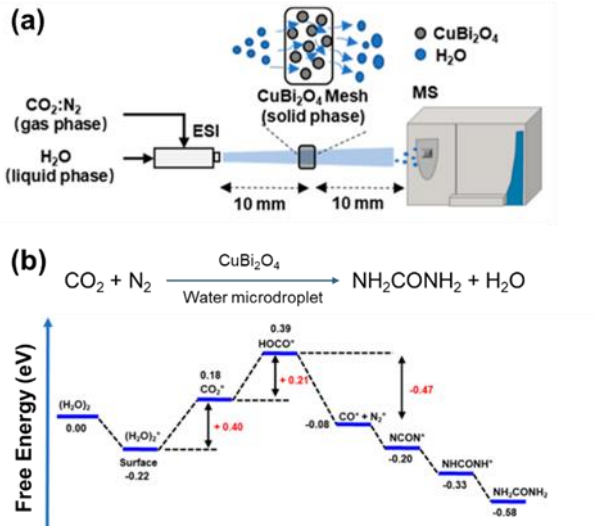


Scheme 8. (a) Water microdroplet promotes the amine-CO_2 coupling with interfacial superacid/base. (b) CO_2 micro-bubbles enhance the amine-CO_2 coupling in water microdroplets.

In another report, it was reported that ammonium bicarbonate (NH_4HCO_3) can apparently enhance the reactions between amines and carbon dioxide (CO_2) in water microdroplets generated by electrospray ionization (ESI).[49] NH_4HCO_3 decomposes into CO_2, generating microbubbles within the microdroplets. These microbubbles serve as internal sources of CO_2, increasing surface area and enhancing the reaction at the liquid-gas interface. This has been confirmed by ^{13}C-labeled NH_4HCO_3 acted as an internal CO_2 source in the reaction. The conversion ratio of amine of N,N-dibutyl-1,3-propanediamine (DBPA, 50 mM in methanol/water) reached 93.7% at a concentration of 20 mM NH_4HCO_3, which is substantially increased. Interestingly, other bicarbonates, such as sodium bicarbonate ($NaHCO_3$) and potassium bicarbonate ($KHCO_3$), were tested but did not achieve the same enhancement in rection as NH_4HCO_3. The findings suggest that NH_4HCO_3 could serve as a superior medium or CO_2 carrier for CO_2 capture and utilization. It provides a potential direction for future CO_2 conversion research.

Urea [$CO(NH_2)_2$], one of the earliest and most important organic molecules synthesized both in the lab and industrially, is produced at a staggering rate of over 190 million tons annually. This production primarily relies on the energy-intensive Haber-Bosch process, which operates under high pressure and temperatures (400-500 K and 150-250 bar), consuming more than 2% of global energy.[50,51] Given the urgency to develop new methods for urea synthesis under milder conditions, a significant breakthrough has been achieved by Zare's group. They demonstrated that nitrogen can be converted into ammonia using water microdroplets combined with a heterogeneous catalyst, a microdroplet gas-liquid-solid multiphase reaction system.[52] Building on this, they reported the one-step formation of urea from CO_2 and N_2 using $CuBi_2O_4$ under water microdroplet conditions. When microdroplet is about 10 μm in size, it creates a 10,000 times larger contact interface. This increased interface allows water microdroplets to more effectively incorporate gas-phase substrates into a heterogeneous reaction system by maximizing contact with a solid catalyst, thereby enhancing catalytic performance compared to dissolution in bulk water. When water (H_2O) microdroplets are sprayed onto a graphite mesh coated with $CuBi_2O_4$, using a 1:1 mixture of N_2 and CO_2 as the nebulizing gas. These microdroplets produce urea [$CO(NH_2)_2$] within 0.1 milliseconds without any external voltage, confirmed by mass spectrometry and ^{13}C nuclear magnetic resonance. The conversion rate reaches 2.7 mmol g^{-1} h^{-1} at 25°C and 12.3 mmol g^{-1} h^{-1} at 65°C. The water microdroplets act as both the hydrogen source and electron transfer medium for the N_2 and CO_2 interacting with $CuBi_2O_4$. The process involves multiple steps: N_2 absorption, N≡N bond cleavage, nitrogen

hydrogenation, and C−N bond formation—occurring at liquid/gas, gas/solid, and liquid/solid interfaces within submillisecond timescales.

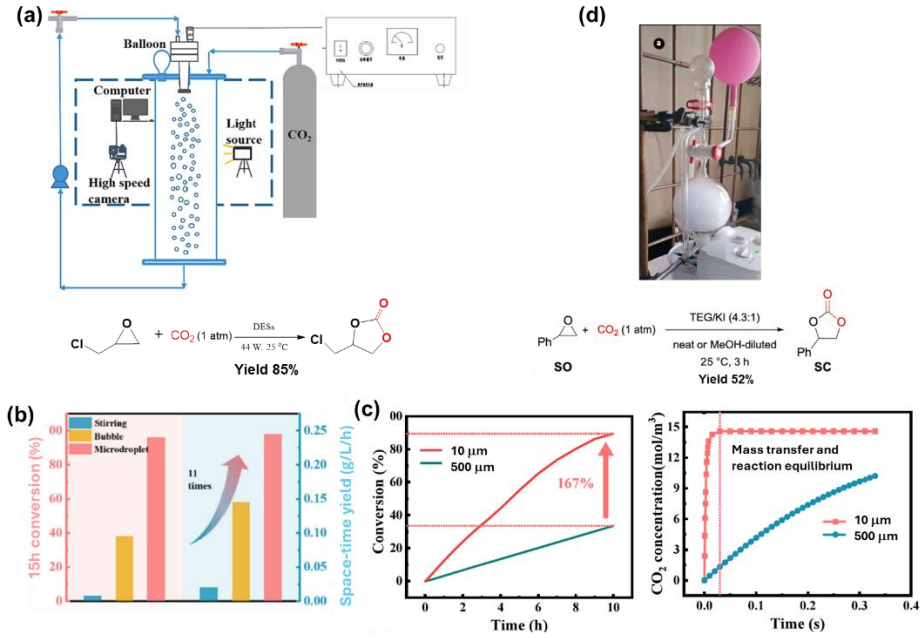


Scheme 9. (a) A setup for multiphase microdroplet reaction system. (b) The direct synthesis of urea from N_2 and CO_2 on $CuBi_2O_4$ catalyst in water microdroplet and its DFT reaction pathway.

The reaction process is likely driven by contact electrification between water and gas, as well as water and solid surfaces. Theoretical insights of the reaction mechanism were studied using DFT calculations with two possible pathways. In one pathway, CO_2 is first absorbed and reduced on the catalyst surface followed by coupling with N_2 (Scheme 9). Water dimers on the surface of the heterostructure afforded the transfer of protons and facile activation of the surface, which triggers the adsorption of CO_2 molecules in the rate-limiting step. The alternative pathway starts from chemisorbing N_2 molecules on the catalyst surface, reducing N_2 to form NH_3 and then coupling with CO_2. $CuBi_2O_4(211)$ surface catalyzes the formation of NH_3 molecules, the rate-limiting step is the first hydrogenation step (N_2 to N_2H). Water microdroplets facilitate physical contact between N_2 and $CuBi_2O_4$, overcome the low solubility of N_2 in water and trig the activation of N≡N triple bond.[53] Herein, water microdroplets serve as both the interaction medium and as proton and electron donors for nitrogen hydrogenation and urea synthesis. This finding offers an exciting eco-friendly approach to producing urea by coupling N_2 fixation with CO_2 utilization without the need for high temperatures, high pressures, or external voltage if the catalyst efficiency and stability, process scalability issues could be overcome in future.

6. Synthesis of cyclic carbonates with CO_2 in microdroplet

The synthesis of cyclic carbonates from CO_2 and epoxides is one of the most well studied reactions and it has been commercialized for polycarbonate synthesis.[54] This reaction has also been validated in microdroplet environment under mild conditions. Zheng et al. presents a novel approach for the highly efficient synthesis of cyclic carbonates through the cycloaddition of CO_2 and epoxides using a circulating microdroplet reactor under atmospheric pressure.[55] The study highlights the use of deep eutectic solvents (DESs), a 1:1 combination of 1-ethyl-3-methylimidazolium iodide and phenol, as catalysts (scheme 10a). This system achieved up to 85% conversion and 99% selectivity of the epichlorohydrin substrate at room temperature. It was found found that increasing the atomizer power from 22 W to 44 W directly correlated with improved substrate conversion due to enhanced droplet formation and smaller droplet sizes. The optimal liquid flow rate was determined to be 9 mL/min, which maximized the gas-liquid interface area without compromising droplet size. A mathematical model was developed to elucidate the intensification mechanism, confirming that increasing the volumetric mass transfer coefficient enhances the dissolution rate of CO_2, thereby improving the overall reaction conversion. The same team has also systematically studied the microdroplet effect on this reaction in a scale-up system and compared with traditional stirring and bubbling systems, scheme 10b and 10c. Microdroplet (10 mm) system demonstrated much higher reaction rate and conversion.[56] In another study, an ultrasonic nebulization reactor was reported on the synthesis of styrene carbonate from styrene oxide (neat or diluted in methanol) using CO_2 and TEG/KI (triethylene glycol/potassium iodide) catalyst, in microdroplet conditions, scheme 10d.[57] The researchers implemented home-made ultrasonic nebulization to create microdroplets, which significantly accelerated the reaction under mild conditions to achieve 52% of yield at 1 atm CO_2 pressure and temperatures of 25°C. It highlights the efficiency of this method compared to traditional bulk reactions.



Scheme 10. (a) The circulating microdroplet system for the conversion of epoxide and CO_2 to cyclic carbonate. (b) Comparison of conversion rate and space-time yield at 15 h among traditional stirring, bubbling and microdroplet reaction systems. (c) Comparison of conversion rates and variation of CO_2 concentration inside the droplet from 0 to 0.3 s between reactions carried on 10 mm and 500 mm droplets. (d) The Ultrasonic microdroplet system for the conversion of styrene oxide to cyclic carbonate. Reproduced from ref. 55 and 57 with permission from Elsevier Ltd, copyright 2024.

The microdroplet reactors in these two examples are self-designed non-electrocharged systems. The results indicated that the simple microdroplet reactor significantly enhances the cycloaddition reaction of CO_2 and epoxides by improving gas-liquid mass transfer. It suggests that microdroplet technology can lead to more efficient CO_2 utilization strategies.

7. Summary and Outlook

Microdroplets, generated through various spray techniques such as electric nebulization, ultrasonic spraying, circular spray, and static droplet formation, exhibit unique properties that make them highly valuable for applications in pharmaceutical synthesis, fine chemicals, and environmental remediation. These microdroplets have distinct interfacial characteristics, including high interfacial tension and the generation of significant electric fields, which result from their large surface area-to-volume ratio. These properties enhance reaction rates and efficiency, as the electric field can influence the alignment and polarization of molecules within the droplet, affecting reaction pathways and product distributions. The charge distribution on

microdroplets also plays a critical role, driving electrochemical processes within the droplet. The presence of an electric field or charge can facilitate the generation of radicals, which are highly reactive species capable of driving complex organic transformations that are challenging in bulk solutions. Additionally, the microenvironment within these droplets can exhibit unique acidic properties due to the concentration of protons at the interface, which can be leveraged in various organic syntheses where protonation steps are crucial. Microdroplets have proven to be powerful tools for CO_2 conversion applications.

Currently, most microdroplet setups operate on a small scale and rely on online mass spectrometry for detection. Despite this limitation, microdroplets hold great potential as efficient tools for reaction screening, particularly for discovering new CO_2 conversion reactions and conditions. In the pharmaceutical and fine chemical industries, microdroplets can function as microreactors, enabling rapid screening of reaction conditions and catalysts, with or without CO_2. Their small volume and unique properties not only accelerate reaction rates and reduce reagent consumption but also facilitate the rapid discovery of novel compounds and synthetic pathways. This capability is particularly beneficial for advancing the process of discovering new CO_2-involved reactions. However, scaling up microdroplet processes remains a significant challenge, especially for CO_2 utilization. The energy input required for droplet formation and maintenance, particularly in methods like electric nebulization or ultrasonic spraying, needs careful optimization. Energy efficiency calculations are crucial to ensure that the benefits of enhanced reaction rates and selectivity are not offset by excessive energy consumption. Furthermore, recent advancements in micro-bubbling technology have been explored to enhance and accelerate various chemical reactions.[58] The application of CO_2 micro-bubbles could also present a fascinating avenue for research in CO_2 utilization.

Despite notable advancements, a comprehensive understanding of the fundamental mechanisms behind accelerated CO_2 conversion in microdroplets remains elusive. Critical aspects, such as the overall mass and energy balances of most microdroplet-promoted reactions, are not yet fully clarified. This aspect, along with life-cycle assessment, requires further investigation to fully address the sustainability concerns surrounding microdroplet-based approaches. Expanding the application of microdroplet technology to areas such as polymer synthesis and degradation, CO_2 conversion into construction materials, and CO_2-assisted degradation of pollutant compounds holds significant potential and could be highly impactful. Moreover, scaling microdroplet chemistry for industrial applications requires significant progress, along with the development of standardized experimental methods and protocols to ensure reproducibility and broader applicability. Microdroplets present a powerful platform for

advancing chemical synthesis and addressing environmental challenges, particularly in CO_2 reduction. Their unique properties offer opportunities to explore novel reaction pathways and enhance reaction efficiencies. Continued research and technological innovations are essential to deepen our understanding of microdroplet processes, paving the way for breakthroughs in CO_2 utilization and fostering innovation across diverse scientific fields.

Acknowledgements

This work was supported by the Institute of Sustainability for Chemicals, Energy and Environment (ISCE2), Agency for Science, Technology and Research (A*STAR), Singapore, and the National Research Foundation, Prime Minister's Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) programme (Development of advanced catalysts for electrochemical carbon abatement), Project Code: 370184872.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

References

[1] Yan, X., Bain, R.M., Cooks, R.G., Organic Reactions in Microdroplets: Reaction Acceleration Revealed by Mass Spectrometry, 2016, Angew. Chem. Int. Ed. 55, 12960-12972. doi.org/10.1002/anie.201602270.

[2] Lee, J.K., Samanta, D., Nam, H.G., Zare, R.N., Micrometer-Sized Water Droplets Induce Spontaneous Reduction, 2019, J. Am. Chem. Soc. 141, 10585−10589. DOI: 10.1021/jacs.9b03227.

[3] Meng, Y., Gnanamani, E., Zare, R.N., Direct C(sp3)–N Bond Formation between Toluene and Amine in Water Microdroplets, 2022, J. Am. Chem. Soc. 144, 19709−19713. doi.org/10.1021/jacs.2c10032

[4] Martins-Costa, M.T.C., Ruiz-López, M.F., Electrostatics and Chemical Reactivity at the Air–Water Interface, 2023, J. Am. Chem. Soc. 145, 1400−1406. doi.org/10.1021/jacs.2c12089.

[5] Chen, X., Xia, Y., Zhang, Z., Hua, L., Jia, X., Wang, F., Zare, R.N., Hydrocarbon Degradation by Contact with Anoxic Water Microdroplets, 2023, J. Am. Chem. Soc. 145, 21538−21545. doi.org/10.1021/jacs.3c07445

[6] Spoorthi, B.K., Debnath, K., Basuri, P., Nagar, A., Waghmare, U.V., Pradeep, T., Spontaneous Weathering of Natural Minerals in Charged Water Microdroplets Forms Nanomaterials, 2024, Science 384, 1012–1017. DOI: 10.1126/science.adl33

[7] Nam, I., Lee, J.K., Nam, H.G., Zare, R.N., Abiotic Production of Sugar Phosphates and Uridine Ribonucleoside in Aqueous Microdroplets, 2017, Proc. Nat. Acad. Sci. 114, 12396–12400. doi.org/10.1073/pnas.171489611

[8] Grooms, A.J., Nordmann, A.N., Badu-Tawiah, A.K., Dual Tunability for Uncatalyzed N-Alkylation of Primary Amines Enabled by Plasma-Microdroplet Fusion, 2023, Angew. Chem. Int. Ed. 62, e202311100. doi.org/10.1002/anie.202311100

[9] Asiri, A.M., Lichtfouse, E., Springer, 2020. https://link.springer.com/book/10.1007/978-3-030-28638-5

[10] Jia, X., Wu, J., Wang, F., Water-Microdroplet-Driven Interface-Charged Chemistries, 2024, JACS Au 4, 4141−4147. doi.org/10.1021/jacsau.4c00804

[11] Wilson, K.R., Prophet, A.M., Chemical Kinetics in Microdroplets, 2024, Annu. Rev. Phys. Chem. 75, 185–208. doi.org/10.1146/annurev-physchem-052623-120718

[12] Hao, H., Leven, I., Head-Gordon, T., Can Electric Fields Drive Chemistry for an Aqueous Microdroplet, 2022, Nat. Commun. 13, 280. doi.org/10.1038/s41467-021-27941-x

[13] Qiu, L., Cooks, R.G., Spontaneous Oxidation in Aqueous Microdroplets: Water Radical Cation as Primary Oxidizing Agent, 2024, Angew. Chem. Int. Ed. 63, e202400118. doi.org/10.1002/anie.202400118

[14] Nam, I., Nam, H.G., Zare, R.N., Abiotic Synthesis of Purine and Pyrimidine Ribonucleosides in Aqueous Microdroplets, 2017, Proc. Natl. Acad. Sci. USA 115, 36–40. doi.org/10.1073/pnas.1718559115

[15] D. Xing, Y. Meng, X. Yuan, S. Jin, X. Song, R.N. Zare, X. Zhang, Angew. Chem. Int. Ed. 2022, 61, e202207587.

[16] Qiu, L., Cooks, R.G., Simultaneous and Spontaneous Oxidation and Reduction in Microdroplets by the Water Radical Cation/Anion Pair, 2022, Angew. Chem., Int. Ed. 61, e202210765. doi.org/10.1002/anie.202210765

[17] Zhang, D., Yuan, X., Gong, C., Zhang, X., High Electric Field on Water Microdroplets Catalyzes Spontaneous and Ultrafast Oxidative C–H/N–H Cross-Coupling, 2022, J. Am. Chem. Soc. 144, 16184−16190. doi.org/10.1021/jacs.2c07385

[18] Xiong, H., Lee, J.K., Zare, R.N., Min, W., Strong Electric Field Observed at the Interface of Aqueous Microdroplets, 2020, J. Phys. Chem. Lett. 11, 7423−7428. doi.org/10.1021/acs.jpclett.0c02061

[19] Wei, Z., Li, Y., Cooks, R. G., Yan, X., Accelerated Reaction Kinetics in Microdroplets: Overview and Recent Developments, 2020, Annu. Rev. Phys. Chem. 71, 31–51. doi.org/10.1146/annurev-physchem-121319-110654

[20] Rennert, K., rank Errickson # 2 , Brian C Prest # 1 , Lisa Rennels # 3 , Richard G Newell 1 , William Pizer 1 , Cora Kingdon 3 , Jordan Wingenroth 1 , Roger Cooke 1 , Bryan Parthum 4 , David Smith 4 , Kevin Cromar 5 6 , Delavane Diaz 7 , Frances C Moore 8 , Ulrich K Müller 9 , Richard J Plevin 10 , Adrian E Raftery 11 , Hana Ševčíková 12 , Hannah Sheets 13 , James H Stock 14 , Tammy Tan 4 , Mark Watson 9 , Tony E Wong 13 , David Anthoff,

et al., Comprehensive Evidence Implies a Higher Social Cost of CO_2, 2022, Nature, 610, 687-692. doi.org/10.5281/zenodo.6932028.

[21] Berner, R.A., The Long-term Carbon Cycle, Fossil Fuels and Atmospheric Composition, 2003, Nature 426, 323−326. DOI:10.1038/nature02131

[22] He, M., Sun, Y., Han, B., Green Carbon Science: Scientific Basis for Integrating Carbon Resource Processing, Utilization, and Recycling, 2013, Angew. Chem. Int. Ed. 52, 9620-9633. doi.org/10.1002/anie.201209384

[23] Francke, R., Schille, B., Roemelt, M., Homogeneously Catalyzed Electroreduction of Carbon Dioxide-Methods, Mechanisms, and Catalysts, 2018, Chem. Rev. 118, 4631−4701. DOI: 10.1021/acs.chemrev.7b00459

[24] Zhuo, Q., Yang, J., Mo, Z., Zhou, X., Shima, T., Luo, Y., Hou, Z., Dinitrogen Cleavage and Functionalization with Carbon Dioxide in a Dititanium Dihydride Framework, 2022, J. Am. Chem. Soc., 144, 6972-6980. doi.org/10.1021/jacs.2c01851

[25] Yu, D., Teong, S.P., Zhang, Y., Transition Metal Complex Catalyzed Carboxylation Reactions with CO_2, 2015, Coord. Chem. Rev. 293, 279-291. doi.org/10.1016/j.ccr.2014.09.002

[26] Zhang, Y., Accelerating CO_2 Conversion Through Microdroplet Chemistry, 2025, Nature Reviews Clean Technology, doi.org/10.1038/s44359-025-00083-9

[27] https://www.mordorintelligence.com/industry-reports/formicacid-Market

https://www.gminsights.com/industry-analysis/formic-acid-market

[28] Song, X., Meng, Y., Zare, R.N., Spraying Water Microdroplets Containing 1,2,3-Triazole Converts Carbon Dioxide into Formic Acid, 2022, J. Am. Chem. Soc. 144, 16744−16748. doi.org/10.1021/jacs.2c07779

[29] Gong, K., Meng, Y., Zare, R.N., Xie, J., Molecular Mechanism for Converting Carbon Dioxide Surrounding Water Microdroplets Containing 1,2,3-Triazole to Formic Acid, 2024, J. Am. Chem. Soc. 146, 8576−8584. doi.org/10.1021/jacs.4c00529

[30] Li, K., Guo, Y., Nizkorodov, S.A., Rudich, Y., Angelaki, M., Wang, X., An, T., Perrier, S., George, C., Spontaneous Dark Formation of OH Radicals at the Interface of Aqueous Atmospheric Droplets, 2023, Proc. Natl. Acad. Sci. U.S.A. 120, e2220228120. doi.org/10.1073/pnas.2220228120

[31] Colussi, A.J., Mechanism of Hydrogen Peroxide Formation on Sprayed Water Microdroplets, 2023, J. Am. Chem. Soc. 145, 16315−16317. doi.org/10.1021/jacs.3c04643

[32] Jin, S., et al., The Spontaneous Electron-Mediated Redox Processes on Sprayed Water Microdroplets, 2023, JACS Au 3, 1563−1571. doi.org/10.1021/jacsau.3c00191

[33] Wang, S., et al., Spontaneously Generated Electrons for CO_2 Hydrogenation to Formate at the Microinterface of Air-Water, 2023, Adv. Energy Mater. 13, 2303121. doi.org/10.1002/aenm.202303121

[34] Dong, J., Chen, J., Wang, W., Wei, Z., Tian, Z.-Q., Fan, F. R., Charged Microdroplets as Microelectrochemical Cells for CO_2 Reduction and C-C Coupling, 2024, J. Am. Chem. Soc. 146, 2227−2236. DOI: 10.1021/jacs.3c12586

[35] Li, J., Chen, G., Zhu, Y., Liang, Z., Pei, A., Wu, C.-L., Wang, H., Lee, H. R., Liu, K., Chu, S., Cui, Y., Efficient Electrocatalytic CO_2 Reduction on a Three-phase Interface, 2018, Nat. Catal. 1, 592–600. doi.org/10.1038/s41929-018-0108-3

[36] Ge, Q., et al., Significant Acceleration of Photocatalytic CO_2 Reduction at the Gas-Liquid Interface of Microdroplets, 2023, Angew. Chem. Int. Ed. 62, e202304189. doi.org/10.1002/anie.202304189

[37] Rodríguez-Jiménez, S., et al., Self-Assembled Liposomes Enhance Electron Transfer for Efficient Photocatalytic CO_2 Reduction, 2022, J. Am. Chem. Soc. 144, 9399–9412. doi.org/10.1021/jacs.2c01725

[38] Vogel, Y.B., et al., The Corona of a Surface Bubble Promotes Electrochemical Reactions, 2020, Nat. Comm., 11, 6323. doi.org/10.1038/s41467-020-20186-0

[39] Mehrgardi, M.A., Mofidfar, M., Li, J., Chamberlayne, C.F., Lynch, S.R., Zare, R. N., Catalyst-Free Transformation of Carbon Dioxide to Small Organic Compounds in Water Microdroplets Nebulized by Different Gases, 2024, Adv. Sci. 11, 2406785. doi.org/10.1002/advs.202406785

[40] Ding, Y., Huang, R., Zhang, W., Huang, H., Nickel-Catalyzed Oxidative Carbonylation of Alkylarenes to Arylacetic Acids, 2022, Org. Lett. 24, 7972−7977. doi.org/10.1021/acs.orglett.2c03121

[41] Meng, Y., Gnanamani, E., Zare, R. N., One-Step Formation of Pharmaceuticals Having a Phenylacetic Acid Core Using Water Microdroplets, 2023, J. Am. Chem. Soc. 145, 7724−7728. doi.org/10.1021/jacs.3c00773

[42] Hryhorczuk, L.M., Novak, E.A., Gershon, S., Gut Flora and Urinary Phenylacetic Acid, 1984, Science 226, 996−996. DOI: 10.1126/science.6438798

[43] Chen, H., Wang, R., Xu, J., Yuan, X., Zhang, D., Zhu, Z., Marshall, M., Bowen, K., Zhang, X., Spontaneous Reduction by One Electron on Water Microdroplets Facilitates Direct Carboxylation with CO_2, 2023, J. Am. Chem. Soc. 145, 2647−2652. doi.org/10.1021/jacs.2c12731

[44] Basuri, P., Mukhopadhyay, S., Prasad Reddy, K.S.S.V., Unni, K., Spoorthi, B.K., Kumar, J.S., Yamijala, S.S.R.K.C., Pradeep, T., Spontaneous α-C−H Carboxylation of Ketones by Gaseous CO2 at the Air-water Interface of Aqueous Microdroplets, 2024, Angew. Chem. Int. Ed. 63, e202403229. doi.org/10.1002/anie.202403229

[45] Banerjee, A., Dick, G.R., Yoshino, T., Kanan, M.W., Carbon Dioxide Utilization via Carbonate-promoted C–H Carboxylation, 2016, Nature 531, 215–219. doi.org/10.1038/nature17185

[46] Chen, C.J., Williams, E.R., The Role of Analyte Concentration in Accelerated Reaction Rates in Evaporating Droplets, 2023, Chem. Sci. 14, 4704–4713. doi.org/10.1039/D3SC00259D

[47] Puxty, G., Rowland, R., Allport, A., Yang, Q., Bown, M., Burns,R., Maeder, M., Attalla, M., Carbon Dioxide Postcombustion Capture: A Novel Screening Study of the Carbon Dioxide Absorption Performance of 76 Amines, 2009, Environ. Sci. Technol., 43, 6427–6433. doi.org/10.1021/es901376a

[48] Huang, K.-H., Wei, Z., Cooks, R.G., Accelerated Reactions of Amines with Carbon Dioxide Driven by Superacid at the Microdroplet Interface, 2021, Chem. Sci. 12, 2242−2250. doi.org/10.1039/D0SC05625A

[49] Feng, L., Yin, X., Tan, S., Li, C., Gong, X., Fang, X., Pan, Y., Ammonium Bicarbonate Significantly Accelerates the Microdroplet Reactions of Amines with Carbon Dioxide, 2021, Anal. Chem. 93, 15775−15784. doi.org/10.1021/acs.analchem.1c03954

[50] Service, R.F., New Recipe Produces Ammonia from Air, Water, and Sunlight, 2014, Science 345, 610. DOI: 10.1126/science.345.6197.61

[51] Lv, C., et al., Selective Electrocatalytic Synthesis of Urea with Nitrate and Carbon Dioxide, 2021, Nat. Sustain. 4, 868−876. doi.org/10.1038/s41893-021-00741-3

[52] Song, X., Basheer, C., Xia, Y., Li, J., Abdulazeez, I., Al-Saadi, A.A., Mofidfar, M., Suliman, M.A., Zare, R.N., One-step Formation of Urea from Carbon Dioxide and Nitrogen Using Water Microdroplets, 2023, J. Am. Chem. Soc. 145, 25910−25916. doi.org/10.1021/jacs.3c10784

[53] Song, X., Basheer, C., Zare, R.N., Making Ammonia from Nitrogen and Water Microdroplets, 2023, Proc. Natl. Acad. Sci. U.S.A. 120, e2301206120. doi.org/10.1073/pnas.2301206120

[54] Guo, L., Lamb, K.J., North, M., Recent Developments in Organocatalysed Transformations of Epoxides and Carbon Dioxide into Cyclic Carbonates, 2021, Green. Chem. 23, 77–118. doi.org/10.1039/D0GC03465G

[55] Zheng, L., Liu, X., Yang, G., Liu, J., Jiang, B., Liu, Y., Li, X., Hu, X., Zhang, Z., Highly Efficient Synthesis of Cyclic Carbonates via Deep Eutectic Solvents from CO_2 at the Gas-liquid Interface of Microdroplet under Atmospheric Pressure Condition, 2024, Chem. Eng. Sci. 289, 119867. DOI: 10.1016/j.ces.2024.119867

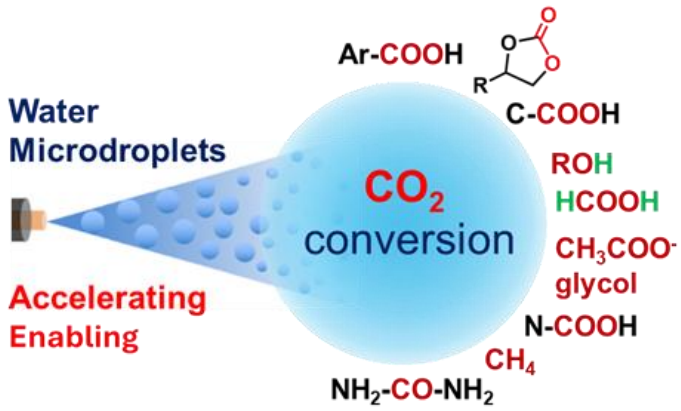
[56] Liu, X., Li, X., Wang, X., Li, Y., Hu, X., Zhou, Z., Zhang, F., Zhang, Z., Chen, Y., Scale-up of Microdroplet Reactors for Efficient CO_2 Resource Utilization, J. Am. Chem. Soc., 2025, 147, 3529–3538. doi.org/10.1021/jacs.4c14733

[57] Urbani, D., Rovegno, C., Massi, A., Leblebici, M.E., Kayahan, E., Polo, E., Dambruoso, P., Efficiency in CO_2-Utilization Strategies: The Case of Styrene Carbonate Synthesis in Microdroplets Conditions, 2023, J. CO_2 Utilization 67, 102328. DOI:10.1016/j.jcou.2022.102328

[58] Bose, S., Mofidfar, M., Zare, R.N., Direct Conversion of N_2 and Air to Nitric Acid in Gas–Water Microbubbles, 2024, J. Am. Chem. Soc., 146, 27964. doi.org/10.1021/jacs.4c11899

Dr. Yugen Zhang is a Senior Principal Scientist at the Institute of Sustainability for Chemicals, Energy and Environment (ISCE^2), A-Star, Singapore. He graduated from the University of Science and Technology of China (USTC, PhD in 1992). He then joined USTC as a faculty and was promoted to Professor in 1999. He visited Riken (Japan) (1996-1997, 2000-2001), where he worked in Prof. Zhaomin Hou' group. Before he joined IBN in 2004, he had been working at Harvard University in Prof. RH Holm's group (2002-2004). His main research areas are green chemistry, nanomaterials and biomaterials.

TOC



Water microdroplets significantly accelerate CO_2 conversion reactions and enable otherwise unfavorable processes due to their unique physicochemical environment—characterized by strong interfacial effects, intrinsic electric fields, localized super acidic or basic conditions, radical formation, and enhanced reducing power.