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Segmented-Flow Microfluidics

Microfluidic Studies of Carbon Dioxide

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carbon dioxide · green chemistry · materials science · microfluidics · supercritical carbon dioxide

Dedicated to Professor George M. Whitesides on the occasion of his 75th birthday

Carbon dioxide (CO_2) sequestration, storage and recycling will greatly benefit from comprehensive studies of physical and chemical gas–liquid processes involving CO_2. Over the past five years, microfluidics emerged as a valuable tool in CO_2-related research, due to superior mass and heat transfer, reduced axial dispersion, well-defined gas–liquid interfacial areas and the ability to vary reagent concentrations in a high-throughput manner. This Minireview highlights recent progress in microfluidic studies of CO_2-related processes, including dissolution of CO_2 in physical solvents, CO_2 reactions, the utilization of CO_2 in materials science, and the use of supercritical CO_2 as a "green" solvent.

1. Introduction

Carbon dioxide (CO_2) as one of the major atmospheric greenhouse gases has the largest contribution to the world climate.[1] Over the past 120 years, due to the increasing anthropogenic CO_2 emission, the concentration of CO_2 in the atmosphere has grown from 280 to 390 ppm,[2] and the amount of CO_2 absorbed by the ocean has been increasing by 2 gigatons of carbon/yr.[3] By the middle of 21st century, the concentration of CO_2 in the atmosphere is expected to double.[2] A continuous increase in CO_2 emission, along with its long atmospheric lifetime,[4] may cause long-term negative effects on the climate. Current climate models and theoretical work suggest that the global annual mean temperature will keep increasing for at least the next two centuries by 3–5 °C/century,[2,3,5–7] which would lead to deglaciation in the arctic regions, the rise of sea levels, flooding, hurricanes and coastal erosion.

Current research and technological strategies directed toward reducing the consequences of CO_2 emission and utilizing gas–liquid systems can be tentatively divided into two groups (Figure 1), namely, 1) capture and storage of CO_2 and 2) applications of captured CO_2. Carbon capture and sequestration involves physical and chemical absorption of CO_2 from flue gas by solvents, followed by the release of CO_2 from the solvent, pressurization and injection of the supercritical CO_2 into underground reservoirs. Currently, post-combustion absorption of CO_2 by solvents is the most extensively used technology for CO_2 capture.[8,9] Examples of solvents physically absorbing CO_2 include dimethyl ethers of polyethylene glycol, methanol, *n*-formylmorpholine, and fluorocarbons. Solvents for chemically mediated CO_2 absorption include alkanolamines, ionic liquids, and aqueous ammonia and potassium carbonate.

Applications of the captured CO_2 include its conversion into fuel,[10–16] plastics[17] and minerals,[18] the use of CO_2 in materials science,[19,20] the utilization of supercritical CO_2 as a solvent[21] and its application in enhanced oil recovery.[22] In particular, the use of CO_2 as a feedstock for the synthesis of an alcohol-based fuel is expected to have high impact, owing to the two orders of magnitude higher worldwide consumption of fuel, compared to other applications.[10,13,15]

The requirements to an efficient solvent for CO_2 capture include low vapor pressure and viscosity, high selectivity for CO_2 uptake, noncorrosive behavior, and negligible environmental impact. Unfortunately, many of currently used solvents are corrosive,[23] and non-selective[24,25] and they also require a large amount of energy (heat) for CO_2 release.[9] These drawbacks necessitate the development of new or optimization of existing solvents for CO_2 sequestration, along with their comprehensive characterization and screening over a range of operating conditions in a labor- and time-consuming process. Conventional macroscale characterization techniques face undesired mass transfer limitation[26,27] and uncertainties in the characterization of CO_2 capture processes, due to poorly defined gas–liquid interfaces. Furthermore, owing to the high rates of physical dissolution and chemical reactions of CO_2, characterization of their kinetic

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and thermodynamic properties by NMR, IR or UV/Vis spectroscopies or pressure decay measurements are cumbersome, and sometimes, impossible.

Recently, microfluidics (MFs) has been successfully used to overcome some of these challenges. In the present Minireview, we highlight the applications of the relatively new (around 14 years) area of research in two-phase MFs for the characterization and screening of CO_2-related processes. We hope that this Minireview will persuade synthetic, environmental and materials scientists and engineers to adapt to the new MF exploratory platforms. It should to be noted that we only focused on CO_2 capture by solvent absorbers and omitted other CO_2 absorption methods, e.g., using membranes[28–30] and microporous materials such as zeolites[31] and metal–organic frameworks.[32,33]

Following the introductory section, in Section 2 we outline the distinct features of droplet MFs, which are pertinent to studies of CO_2-related processes. Microfluidic studies of physical and chemical absorption of CO_2, applications of CO_2 in materials science and of the supercritical CO_2 are reviewed in Section 3. We conclude with an outlook discussing perspectives of the applications of MFs in studies of CO_2 capture and sequestration.

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2. Introduction to Droplet Microfluidics

Microfluidics is the science and technology of phenomena that involve motion of fluids through or past structures with dimensions less than 1 mm.[34,35] Over the past decade or so, MFs has emerged as a promising tool for fundamental and exploratory studies of chemical reactions, e.g., fluorination,[36,37] bromination,[38] hydrogenation,[39,40] the synthesis of polymers,[41–44] and the generation of polymer[45–48] and inorganic[49] particles. Advantages of MFs include 1) rapid heat and mass transfer; 2) small reagent volumes (important for expensive and hazardous reagents); 3) the ability to conduct multi-step reactions without exposure of reactive intermediates to ambient conditions; 4) the capability to vary reagent concentrations in a high-throughput manner by changing their volumetric flow rates; and 5) the capability of integration of analytical tools with MF reactors for real-time characterization.

Flow of fluids in MF reactors can occur in a single-phase or a multi-phase state. In the single-phase co-flow of miscible fluids, the parabolic velocity profile leads to relatively slow mixing. Moreover, the spread of solute molecules along the direction of flow limits spatial control over reagent concentrations for high-throughput screening applications. Multiphase flow includes either co-flow of immiscible liquids in a continuous manner, or the discontinuous flow of droplets of one fluid within the continuous phase of the other one (called droplet MFs).[50–53] Recently, droplet MFs has been extended to studies of gas–liquid physical processes[54–60] and chemical reactions,[61–64] in which droplets were replaced with gas bubbles.[65] Generally, bubbles had diameters equal to the microchannel diameter and lengths exceeding the microchannel width, thereby forming gaseous plugs (Figure 2). These systems exhibited a narrow and controllable distribution of sizes of gaseous plugs and liquid segments between them, well-defined gas–liquid interfaces, reduced axial dispersion,[65–67] enhanced mixing, and reduced mass transfer resistance, due to the formation of two stirring zones in segments of the continuous phase (shown with arrows in Figure 2). This MF approach, called gas–liquid segmented flow (Figure 2), enabled one to overcome the limitations of conventional studies of gas–liquid processes and provided valuable information on CO_2 diffusion coefficients,[60,68,69] gas solubility,[54–56,60] reaction kinetics[61] and thermodynamics,[62] and adsorption of particles to CO_2–liquid interfaces.[19,20,70–74] In summary, three important advantages of MF technologies in studies of gas–liquid processes, including CO_2-related processes, compared to macroscale techniques include 1) the unique ability to measure and reduce the gas–liquid mass transfer time, owing to small dimensions and precise control over the size of the gas bubbles and liquid segments, 2) high-

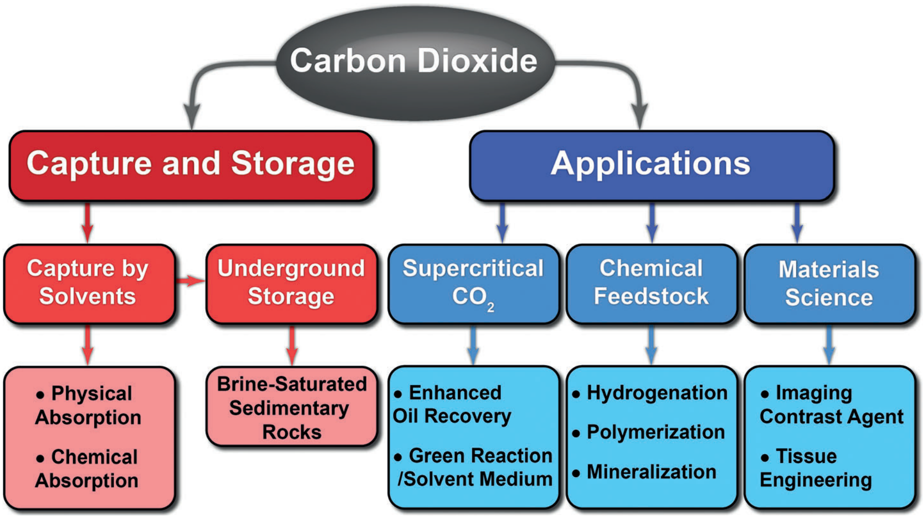

Figure 1. Current research and technological routes towards capture, storage and chemical recycling of CO_2 using gas–liquid interactions. Carbon dioxide captured by absorbent solvent, is released, pressurized and injected into an underground reservoir.

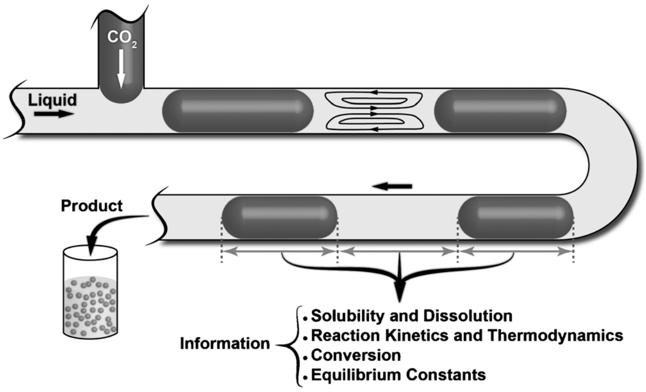

Figure 2. Schematic of segmented flow for gas–liquid processes involving CO_2. Plugs of CO_2 (shown with dark color) undergo shrinkage governed by the dissolution in or reaction with the adjacent liquid segments (shown with light gray color), until the size of CO_2 plug is stabilized.

throughput screening of the parameter space of chemical reactions and physical processes, and 3) the real-time characterization of the gas–liquid processes, due to the ability to access the gas–liquid physical or chemical process at a particular moment of time.

Current MF studies of CO_2 can be divided into two major categories: 1) experiments that utilize time-dependent reduction in volume of gaseous CO_2 plugs, due the transfer of CO_2 molecules in adjacent liquid segments (Figure 2) and 2) experiments conducted with supercritical CO_2 (sc-CO_2) without optically detectable shrinkage of sc-CO_2 droplets (and sometimes, using sc-CO_2 in a single-phase configuration). Most MF studies within the first category have focused on the exploration of physical dissolution of CO_2 in aqueous[56,57,75] or organic[54,55,58] solvents. We note that although CO_2 reacts with water, because of the small value of the equilibrium constant (4.4×10^{-7} at pH < 10[76]), it can be assumed that the dominant species in the aqueous solution are the physically dissolved CO_2 molecules.

The second group of studies focused on CO_2 reaction kinetics, conversion, thermodynamics and optimization of reaction conditions.[61,62] The third group of experiments utilized dissolution of CO_2 bubbles and accompanying increase in acidity of the aqueous liquid in the neighborhood of the bubbles to generate stable microbubbles covered with colloidal particles,[19,70,73,74] polymers[72] or cells[20], with potential microbubble applications as imaging agents,[19] tissue engineering and site-specific drug delivery vehicles. The last group of CO_2-related studies targeted the applications of sc-CO_2[56] as a green solvent for extraction[77] and hydrogenation,[39,78–80] as well as a co-solvent in nanomaterial synthesis.[80–82]

3. Advances in Microfluidic Studies of CO_2

3.1. Dissolution of CO_2 in Physical Solvents

Studies of physical dissolution of CO_2 can be considered as the vital first step towards studies of CO_2 reactions,[83] however, they are also important in their own right by facilitating the design of efficient physical solvents for CO_2 sequestration. A gas-impermeable silicon-based MF device was utilized to study CO_2 dissolution in methanol, ethanol and water by monitoring the reduction in dimensions of CO_2 plugs immediately after their generation.[59] The shrinkage of CO_2 plugs over time t, exhibited two regimes: a fast diffusive regime ($t < 1$ ms), in which the reduction in CO_2 plug volume was proportional to t^1, and a slow diffusive regime for $t > 1$ ms, in which volume reduction was proportional to $t^{1/2}$. The transition between the two regimes occurred due to the decreased CO_2 concentration gradient across the gas–liquid interface, due to the buildup of CO_2 concentration in the liquid. By employing a one-dimensional mass transfer model with experimental results, it was shown that the initial dissolution rate of CO_2 plugs increases at higher CO_2 inlet pressure, higher CO_2–liquid diffusivity, and lower Henry's law coefficient. This work necessitated a systematic examination of the dependence of gas–liquid mass transfer on velocity of gas plugs, viscosity of the liquid, and the volume of liquid segments. An automated MF platform was developed to image and analyze time-dependent shrinkage of CO_2 plugs.[54] By imaging a 8×12.5 mm region of interest (shown with a red frame in Figure 3a), ca. 20000 CO_2 plugs were detected and their dimensions were analyzed using a custom-developed MATLAB image processing code. After accounting for expansion of CO_2 plugs due to the pressure drop along the microchannel, the reduction in plug volume was converted into the concentration of the dissolved CO_2 in the liquid. In the next step, gas–liquid mass transfer was examined using an image-based feedback method for controlling the interdependent flow characteristics such as the lengths and velocities of gas and liquid segments,[55] thereby replacing their manual time-consuming and setup-dependent adjustment.[52,53] It was found that gas–liquid mass transfer was enhanced, due to improved stirring in the recirculation zones in liquid segments (Figure 2), and thus with increasing initial velocity, U_{B0}, of gas plugs. Figure 3b shows the reduction of mass transfer time, t_{MF}, with increasing U_{B0}, that is, the ability to tune and minimize t_{MF} in the MF studies of CO_2. Furthermore, by comparing the initial and equilibrium volumes of CO_2 plugs, the solubility of CO_2 in dimethylcarbonate (DMC) at different temperatures was measured and validated against the reported Henry's law coefficients (Figure 3c). A similar MF method was used to determine the diffusivity and solubility of CO_2 in other solvents, including poly(ethylene glycol), 1-octanol, 1-methyl-2-pyrrolidinone, propylene carbonate and 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl) imide.[60] Fast (ca. 5 min per system) screening of CO_2 uptake was also achieved for solvent mixtures with varying compositions, while similar experiments conducted in the bulk would have required days.[84,85] Monitoring the CO_2 volume reduction has also been utilized to study mass transfer in "bubbly flow", that is, in a liquid carrying bubbles with diameters smaller than microchannel dimensions.[86] Bubbles containing a mixture of CO_2 and N_2 were generated in the solution of monoethanolamine (MEA) and ethylene glycol. The coefficient of gas–liquid mass transfer increased with increasing CO_2 volume fraction in the bubbles and with increasing flow rate of the liquid. The initial gas dissolution during the formation of the bubble (within 5 ms) led to 25–50% of the overall gas–liquid mass transfer in the MF device.

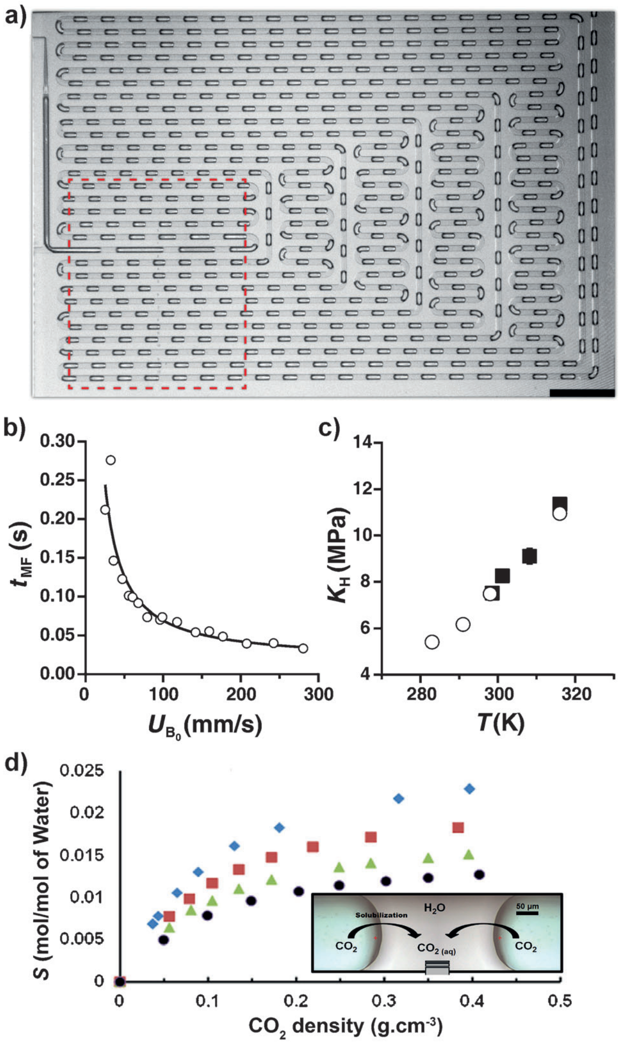

Figure 3. a) Bright-field image of CO_2 plugs undergoing dissolution in a physical solvent (DMC).[54] The imaged area of interest is highlighted with a red frame. Scale bar is 3 mm. b) Experimentally measured mass transfer time for of the CO_2 plug and DMC slug lengths, over one order of magnitude of the variation in the initial gas plug velocity.[55] c) Temperature-dependent CO_2–DMC Henry's constants measured in the automated gas–liquid segmented flow microreactor (○) and validated vs. reported literature values (■).[54] d) Solubility of CO_2 in salty water, plotted as a function of CO_2 density (adjusted by the applied pressure) at NaCl concentration of 0 (◆), 1 M (■); 2 M (▲) and 3 M (●). Inset shows a bright-field micrograph of CO_2–brine segmented flow.[56] Scale bar is 50 µm. Reproduced with permissions from the Royal Society of Chemistry, 2012 (a–c) and from Elsevier, 2012 (d).

Studying CO_2 uptake by aqueous systems is of tremendous importance, since the ocean is the largest sink of CO_2.[87–89] In addition, the underground storage of CO_2 takes place in reservoirs that are formed by sedimentary rocks saturated with salty water (brine). Field studies of CO_2 dissolution and solubility are expensive and time-consuming, while MF platforms enable high-throughput studies of CO_2 uptake by water under different salinity and temperature conditions. Since the solubility of CO_2 in water reduces with increasing temperature, CO_2 bubbles passing through consecutive cold, hot and cold regions of the MF device, exhibited the corresponding shrinkage-expansion-shrinkage behavior, due to the flux of CO_2 from and to the bubbles, thereby mimicking CO_2 dissolution at high and low altitudes.[75] A decreased uptake of CO_2 was measured in aqueous NaCl solutions and ocean water extracted from Bermuda coastal waters, compared to the deionized water, due to the increased contribution of an ionic strength of water in CO_2 dissolution.[75,90,91] In another study, high-pressure MF studies of CO_2-brine systems aimed at the examination of the combined effects of pressure and salt concentration on CO_2 solubility and diffusivity.[56] A high pressure-compatible MF reactor was integrated with in-situ confocal Raman spectroscopy. The CO_2-brine flow was stopped, and the intensity of the band corresponding to the physically dissolved CO_2 molecules in brine (an aqueous CO_2 Fermi dyad band) was monitored in time as a function of pressure and salt concentration. The CO_2 solubility in brine decreased with increasing salt concentration (Figure 3 d). This work provided the ability to measure CO_2 solubility at pressures and temperatures corresponding to sc-CO_2, when optical microscopy failed to monitor CO_2 plug shrinkage, however it required calibration for CO_2 Raman spectrum intensity vs. CO_2 concentration. In another MF platform, CO_2 diffusion in brine at different salt concentrations was studied under the pressure of up to 5 MPa by monitoring CO_2-mediated fluorescence quenching of the tracer introduced in the brine.[69] The CO_2-brine diffusivity was inversely proportional to the concentration of salt in the brine.

Another important area of research concerns CO_2 injection under high pressure (up to 10 MPa) into deep, heavy and viscous oil (bitumen) to facilitate oil recovery.[22] The process is governed by the mass transfer rate and diffusivity of CO_2 into bitumen. Conventional CO_2–bitumen mass transfer characterization methods[92–94] are labor- and time-consuming, while small-scale diffusion lengths, characteristic for two-phase MFs, can greatly benefit studies of CO_2 mass transfer in heavy oil. One-dimensional swelling of a stationary bitumen plug was used to evaluate the diffusion coefficient of CO_2 in bitumen under high pressure.[68]

3.2. Microfluidic Studies of CO_2 Reactions

Chemical CO_2 sequestration and its potential conversion into a fuel fuel offers a sustainable solution to the global extra emission of CO_2.[13] However, owing to the thermal stability and low reactivity of CO_2, its utilization as a C_1 chemical feedstock to produce carbon monoxide[95] or renewable fuels such as methanol[13–15] remains a challenge. Currently, aqueous amines are extensively used for CO_2 capture.[8,9] Two challenges associated with these systems are the relatively high energy for regeneration of the solvent by releasing the captured CO_2, and the oxidative degradation of the solvent, due to the presence of oxygen in the flue gas.[23,25] The development of new chemical systems and optimization of existing formulations for chemical CO_2 sequestration require fundamental characterization of the kinetics and thermodynamics of CO_2 reactions. For fast reactions occurring on the time scales from milliseconds to seconds, inaccurate measurements of gas–liquid mass transfer time can lead to large uncertainties in measured reaction rates.[96–98] When the mass transfer time is comparable with or longer than the reaction time, the experimentally measured reaction kinetics will be mass transfer-limited, and will not represent the reaction rate. To accurately measure the kinetics of gas–liquid reaction, the ratio of gas–liquid mass transfer timescale over the reaction timescale (that is, the reaction rate over the mass transfer rate), known as Damköhler number, Da, should be significantly smaller than 1.

In addition, conventional reaction characterization techniques are time-consuming and require relatively large amounts of reagents. Moreover, conventional spectroscopic characterization may fail to evaluate large reaction equilibrium constants, when the concentration of reagents at the equilibrium is below the detection limit.[99] A MF platform was utilized in fundamental studies of the reaction of CO_2 with frustrated Lewis pairs (FLPs).[62] These reagents reversibly bind to CO_2 under mild temperatures and pressures and their unquenched reactivity can be used for metal-free catalysis of CO_2 hydrogenation.[100–102] These properties of FLPs make them an excellent candidate for the next generation of chemical CO_2 absorbers. Experiments with tri-*tert*-butylphosphine, *t*Bu_3P, and chloro-bis(pentafluorophenyl) borane ($ClB(C_6F_5)_2$) are shown in Figure 4 a.[62] The MF methodology relied on the comparison of the total

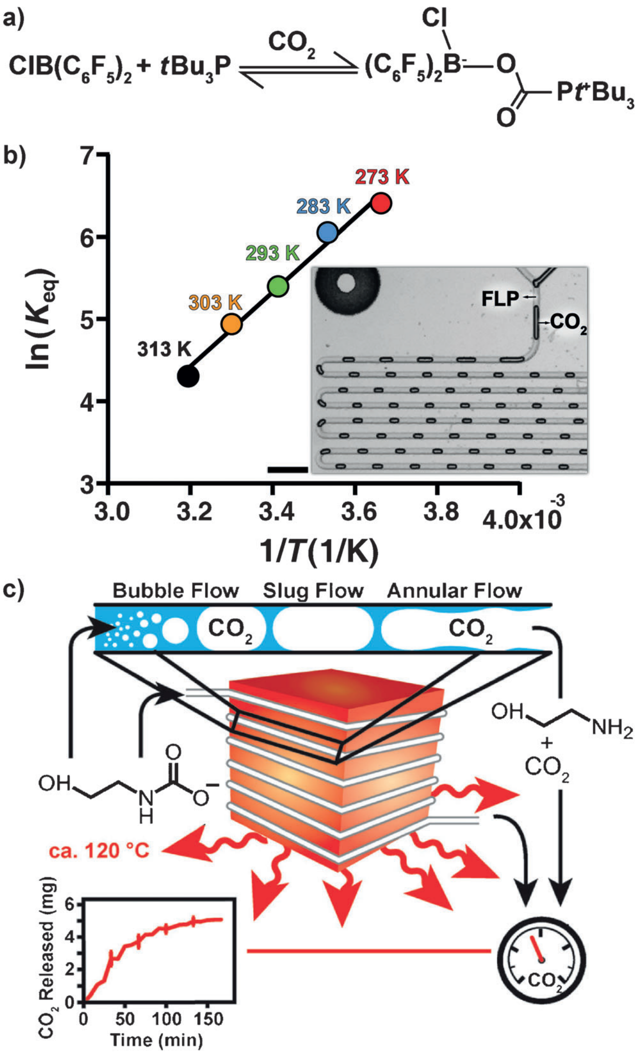

Figure 4. a) Reversible CO_2 binding with the FLP reagents in bromobenzene solvent.[62] b) Experimentally measured CO_2–FLP equilibrium constants at different temperatures using the MF segmented flow-based strategy. The inset shows a typical bright-field CO_2–FLP segmented flow image obtained using a glass-based microreactor. Scale bar is 1 mm.[62] c) Schematic of the proposed CO_2 stripping process from saturated MEA by flowing through a microchannel patterned around a heat source. The released CO_2 formed bubbles in the microchannel.[63] Reprinted with permission from the American Chemical Society, 2014 (a,b) and from Wiley-VCH, 2013 (c).

amount of CO_2 physically uptaken by the solvent (bromobenzene) and the solution of FLP reagents in bromobenzene. Based on van't Hoff's law, the results of MF experiments provided the values of equilibrium constants of CO_2–FLP reactions at different temperatures (Figure 4b), as well as the enthalpies, entropies, and Gibbs free energies of these reactions.

Another area of research that can greatly benefit from MF studies is related to switchable solvents,[103] whose polarity,[104,105] ionic strength,[106] hydrophilicity,[107] or viscosity[108] can be reversibly changed ("switched") upon injection of CO_2 in the system, due to the reaction of CO_2 with a nitrogeneous base in the solvent. The original solvent can be recovered by applying heat or by purging an inert gas to release CO_2. The reversible change in solvent properties offers a sustainable strategy for multistep processes requiring different solvent properties in different steps. A MF platform was utilized for studies of the kinetics of the reversible binding of CO_2 to a secondary amine by comparing the time-dependent shrinkage of CO_2 plugs in the solution of *N*-ethylbutylamine in acetonitrile with that in pure acetonitrile.[61] Although validation of the MF approach by applying it to the well-established CO_2–MEA reaction was successful, further investigation of the nonlinear gas–liquid mass transfer behavior, when comparing a pure solvent with the reactive system, is needed.

One of the most energy-consuming stages of CO_2 sequestration is the release of captured CO_2 from the solvent by heating (a stripping process). The heat required to release the captured CO_2 is supplied using electricity or combustion of fossil fuels. Yet, waste heat at the surface of combustion vessels in power plants can be utilized for the stripping process. This approach was tested by fabricating a microchannel around a heat source, in order to study the CO_2 release rate and the total amount of released CO_2 from MEA for different microchannel geometries and heat source temperatures (Figure 4c).[63] Upon transfer of CO_2 from the CO_2-saturated MEA, small CO_2 bubbles appeared in the MEA solution. The CO_2 removal rate and the total amount of the released CO_2 were measured with an infrared CO_2 meter and a gas mass flow-meter, and were further confirmed by optically monitoring the volume and the flow rate of the released CO_2 plugs in the microchannels.

3.3. Carbon Dioxide and Materials Science

In addition to being an exploratory tool for CO_2-related processes, MF generation of highly monodisperse CO_2 bubbles and their controllable dissolution offer an attractive platform for the generation of small, stable and biocompatible bubbles for imaging-based medical diagnostics and therapeutics[19,70–74]. Small gas bubbles are highly echogenic, due to the large difference in their compressibility and density, compared to the liquid medium. A strong ultrasound (US) scattering by microbubbles occurs also because of their asymmetric oscillations and can thus improve the contrast of US imaging by resonating with the US waves.[109,110] Conventional microbubble preparation techniques utilize sonication and multi-step layer-by-layer biopolymer deposition on the bubble surface,[111,112] which provide insufficient control over bubble sizes.

The MF strategy shown in Figure 5a employed 1) the MF generation of bubbles from a mixture of CO_2 with a minute amount of a low-soluble gas in an aqueous biopolymer

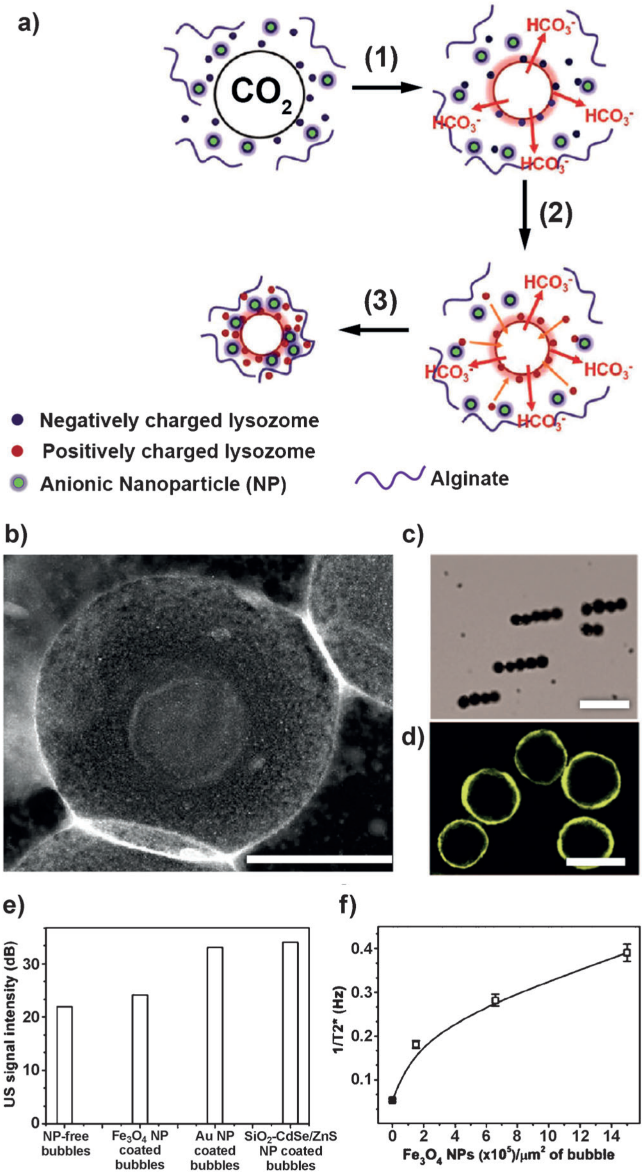

Figure 5. a) Formation of CO_2 bubbles functionalized with anionic NPs and a lysozyme–alginate layer.[19] b) Scanning transmission electron microscopy (STEM) image of the surface of the CO_2 bubbles covered with the lysozyme–alginate shell and loaded with Au NPs. Scale bar is 6 μm.[19] c) Bright-field image of the magnetic actuation of the bubbles coated with Fe_3O_4 NPs. Scale bar is 5 μm.[19] d) Confocal microscopy image of the bubbles coated with CdSe/ZnS quantum dots encapsulated within carboxylated silica. The scale bar is 100 μm.[70] e) Enhancement of the ultrasound signal over background for different types of functionalized bubbles.[19] f) Evolution of MRI relaxation rate as a function of surface density of Fe_3O_4 NPs deposited on the surface of bubbles. The concentration of CO_2 in all experiments was 10^4 CO_2 bubbles/mL.[19] Reprinted with permission from the American Chemical Society, 2010.

solution and/or a dispersion of surface-carboxylated nanoparticles (NPs), 2) the rapid dissolution of CO_2, leading to the dramatic bubble shrinkage and an increase in the acidity of the solution in the vicinity of the bubble surface, and 3) the deposition of the polymer and/or NPs at the gas–liquid interface in the process driven by the chemically mediated change in NP surface energy.[19,70,73,113] The size of the bubbles was tuned by varying the fraction of the low-soluble gas, the initial bubble size, the temperature,[73,75] and the flow rate and the pH of the liquid phase. Small 7 μm-diameter biopolymer-encapsulated bubbles have been reported[72] that did not change their size and stability over at least, 3 months. Functionalization of the bubble surface with metal (Au), semiconductor (CdSe/ZnS) and metal oxide (Fe_3O_4) NPs enabled additional imaging modalities based on plasmonics, fluorescence, and magnetic resonance imaging (MRI), respectively.[111,115,116] Figure 5b–d show the versatility of the MF approach for the encapsulation of small, monodisperse bubbles with an alginate–lysozyme shell loaded with Au, Fe_3O_4 and SiO_2-encapsulated CdSe/ZnS NPs, respectively. The NP-functionalized CO_2 bubbles enhanced the US imaging intensity (Figure 5e).[19] Moreover, in vitro MRI experiments showed that the negative contrast in MRI imaging was enhanced and relaxation rates increased with increasing surface density of Fe_3O_4 NPs (Figure 5f). This MF strategy was further extended to the encapsulation of CO_2 bubbles within a shell of carboxylated particles at different temperatures, in order to avoid the need in pH change to control bubble size.[73] A similar platform was employed for the preparation of CO_2 bubbles coated with yeast cells,[20] called yeastosomes,[117] which could potentially be used as the building blocks in tissue engineering.[118] Bubbles of CO_2 were generated in an aqueous solution containing yeast cells coated with poly(allylamine hydrochloride). A 16% polydispersity of the cell-loaded bubbles necessitated further characterization and optimization of the MF approach towards more uniformly sized cell-coated bubbles.

Compared to other gases such as perfluorobutane[114] or air, which would require a three-step process for nanoparticle/polymer deposition on microbubble surface, the utilization of the dissolution of CO_2 provided a single-step assembly of polymer/particles at the gas–liquid interface. While, in principle, other highly soluble gases reacting with water with an accompanying strong local change in pH could be used. Gas selection depends on their cost, toxicity, the design of polymer and nanoparticles depositing at gas–liquid interface and other factors.

3.4. "Green" Chemistry: Supercritical CO_2

Over the past three decades, sc-CO_2 has drawn a lot of attention in synthetic chemistry as a "green" reaction medium[21] (although its use as an environmentally benign solvent would only be justified by evaluating its long-term environmental impact). Supercritical CO_2 (critical temperature of 304.25 K, critical pressure of 7.39 MPa) has been utilized as a solvent or a co-solvent for gas or organic compounds,[119,120] in catalytic hydrogenation[22,121,122] and polymerization[123] reactions, extraction of organic solutes,[124–126] and the synthesis of inorganic NPs.[127–130] These processes were conducted at high pressures and temperatures with an insufficient optical access to the fluids. The products were characterized, after the reaction was complete, by conventional spectroscopy or electron microscopy techniques. With the advent of MF reactors compatible with high (up to 400 °C) temperatures and pressures of up to 40 MPa,[131,132] advantages of microscale systems such as enhanced rates of heat and mass transfer and real-time reaction characterization were used for chemical processes involving sc-CO_2.[56,77–79,81,82,132–135]

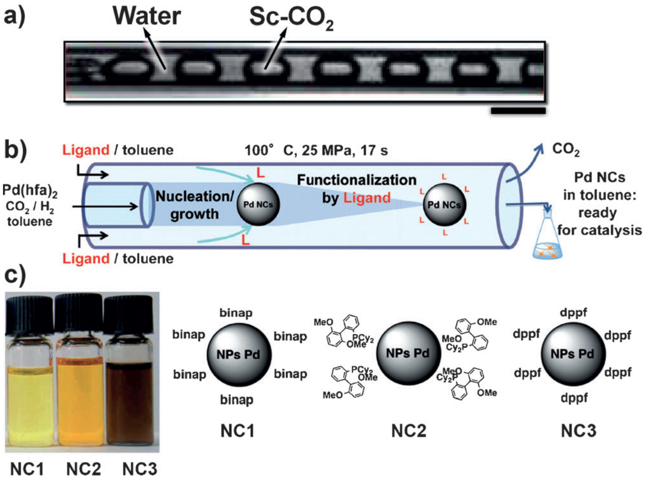

Figure 6. a) A bright field image of sc-CO_2 droplets dispersed in water in a silica capillary. Scale bar is 400 μm.[133] b) Schematic of the experimental setup utilized for synthesis of Pd NCs using toluene–sc-CO_2 mixture as the solvent.[82] c) Three types of Pd NCs dispersed in toluene with their corresponding surface capping.[82] Adapted from Ref. [82] with permission from Wiley-VCH, 2012.

A silica capillary MF reactor (Figure 6a) was employed to study the dynamics of sc-CO_2 emulsification in water and a pressure-controlled transition from the dripping to the jetting mechanism of sc-CO_2 droplet formation. This work demonstrated another advantage of the MF platform, that is, the ability to adjust sc-CO_2 density, viscosity and diffusivity by inducing a relatively small temperature or pressure gradient, while visualizing the physical (e.g., extraction) or chemical (e.g., hydrogenation) process. A MF platform (Figure 6b), in a co-flow configuration, was utilized for the MF synthesis of palladium (Pd) nanocrystals (NCs) in toluene at 100 °C and 25 MPa. The solubility of hydrogen in toluene, used for the reduction of the Pd^{II} precursor, bis(hexafluoroacetylacetonate) palladium(II), was increased by using sc-CO_2 as a co-solvent. Examination of the catalytic activity of Pd NCs coated with ligands with different electronic and steric properties, such as 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (NC1), 2-dicyclohexyl-phosphino-2,6′-dimethoxybiphenyl (NC2), and 1,1′-bis(diphenyl-phosphino) ferrocene (NC3) showed that the sample NC3 was the best catalyst leading to > 99% conversion and 96% reaction yield for Vaultier borylation reaction. This example highlights the advantages of high-pressure and high-temperature MF studies for screening and optimization of the synthesis of NCs for catalytic reactions. Multiphase MFs was also used for extraction of vanillin from water by sc-CO_2.[77] The efficiency of extraction was strongly enhanced with increasing pressure (and thus the density of sc-CO_2). We note that while some of MF studies of sc-CO_2 were conducted using segmented flow and co-flow configurations, other MF experiments of sc-CO_2 such as catalytic hydrogenation[39,40,78,79] and esterification reactions [132] were performed in a single-phase flow configuration, due to the high diffusivity of sc-CO_2 and comparatively weak axial dispersion.

4. Summary and Outlook

Carbon dioxide capture, storage, temporary sequestration, conversion into a fuel and applications in green chemistry and materials science—all require real-time information on the gas–liquid mass transfer process. Recent advances in the application of MFs to studies of CO_2-related physical and chemical processes have demonstrated benefits of microscale approaches, in which the rates of heat and mass transfer are superior to their macroscale counterparts. Microfluidic platforms offered a high-throughput, labor- and time-efficient screening of chemical formulations and operation conditions on the conversion rate, uptake and thermophysical properties of CO_2.

Owing to the difference in the length scales of micro- and macroscale systems, the higher heat and mass transfer rates associated with MF systems, compared to their analogous macroscale systems, may not be directly used for industrial-scale continuous processes, unless both systems operate at similar regimes of $\mathrm{Da} \ll 1$, where the mass transfer timescales are much smaller than reaction timescales. However, irrespective of the Da regime, reaction rates, thermodynamic characteristics, and equilibrium constants can always directly be transferred to macroscale CO_2 reactions. Moreover, the screening of the reaction parameter space and optimization of chemical formulations can be performed within significantly shorter times (10–100 conditions/hour) by using a smaller amount of reagents and solvents (ca. 5 μL/condition), compared to the macroscale screening. In addition to expensive MF devices fabricated in glass or silicon, cost-efficient development of other materials, e.g., polymers,[136] with a high transparency, chemical resistance to organic solvents and a low gas permeability, would benefit CO_2-related MF research, although MF experiments would be performed at moderate gas pressures and temperatures

We note that MFs on its own will not solve the problems of anthropogenic CO_2 emission, however, exploratory MF platforms can bring new fundamental knowledge on CO_2 related processes and facilitate the development of more efficient CO_2 capturing agents. We envision that the utilization of MFs would accelerate the development of new catalysts for CO_2 conversion into useful products such as fuel (e.g., methanol)[13,14] or minerals (e.g., calcium carbonate).[18] Moreover, we foresee that MF platforms will be applicable to characterization and screening of CO_2 capture by using membranes[28–30] and microporous materials.[32,33]

Segmented-flow MFs is a fairly new research field and although it has the potential to become an efficient tool in studies of CO_2, a number of questions remain to be addressed. For example, the effect of local temperature rise, due to the exothermic nature of CO_2 reactions, should be examined by employing local temperature probes. An undesired local increase in temperature can be counteracted by selecting good thermoconductors (e.g., silicon) for the fabrication of MF reactors. A common concern for exothermic gas–liquid reactions is the local temperature profile within the liquid (particularly hot spots at the gas–liquid interface, and associated generation of side products). Increasing the flow velocity would be one way to reduce that effect.

Another important question is the possibility of communication between flowing liquid segments separated with shrinking CO_2 plugs. This effect may take place due to the presence of thin liquid film surrounding gaseous plugs and may cause the distribution of the dissolved CO_2 between the liquid segments. Surface treatment of the walls of the MF reactors can significantly reduce this effect by suppressing the formation of the liquid film around the plugs.[137] The contribution of the gas–liquid mass transfer during the formation of gas plugs to the overall gas–liquid mass transfer, the nonlinear gas–liquid mass transfer behavior in reactive (solvent + reagent) systems and the corresponding change in volume of liquids should be further investigated.

In addition, studying the underground injection and transport of sc-CO_2 for CO_2 storage and enhanced oil recovery is of great importance, and high-pressure MF platforms have recently enabled better understanding of the mechanisms involved in this process.[137,138] Studies conducted in high (up to 40 MPa) pressure-compatible MF devices fabricated in silicon or glass[131] can facilitate better understanding of microscale fluid transport on length scales similar to the pore sizes of underground sedimentary rocks and benefit real-world efforts on CO_2 storage.

There are many other areas in CO_2-related research that can benefit from the exploratory MF platforms, including the introduction of metal (Ni) NPs in water to increase CO_2 solubility and produce carbonic acid,[18] or addition of metal NPs in sc-CO_2 during its underground injection to enhance convective mixing with brine and reduce the risk of potential leakage.[139] Moreover, studies of CO_2-mediated processes occurring in switchable solvents, e.g., liquid–liquid phase separation or extraction[104–108,140] can be explored and screened by using MF platforms. Microfluidic strategies can also be extended towards studies of other reactive gases such as CO or H_2, as well as electrochemical reduction of CO_2[141] to liquid fuels as another promising route for conversion of CO_2 to valuable products.

On the other hand, MF technologies can be used in materials science to produce high-value products. For example, owing to the high frequency (up to kHz) generation of highly monodisperse bubbles, scaled-up MF platforms can be envisioned as microfactories for continuous production of polymer-encapsulated bubbles that can be used as contrast agents for ultrasound imaging and treatment (with a typical concentration of 1×10^9 microbubbles mL^{-1}),[109] in drug delivery, aerated food, and cosmetics.

Despite the numerous advantages offered by MF platforms, there is a very small number of synthetic chemistry or materials science groups that are already utilizing this technology for exploration and screening of gas-liquid processes. We hope this Minireview will extend the utilization of these systems, and open the doors for future collaborations between engineers and synthetic chemists.

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