Catalytic Carbon Capture: A Low-cost Climate Change Mitigation Strategy

Shrey Khetan
Princeton High School
March 12, 2023

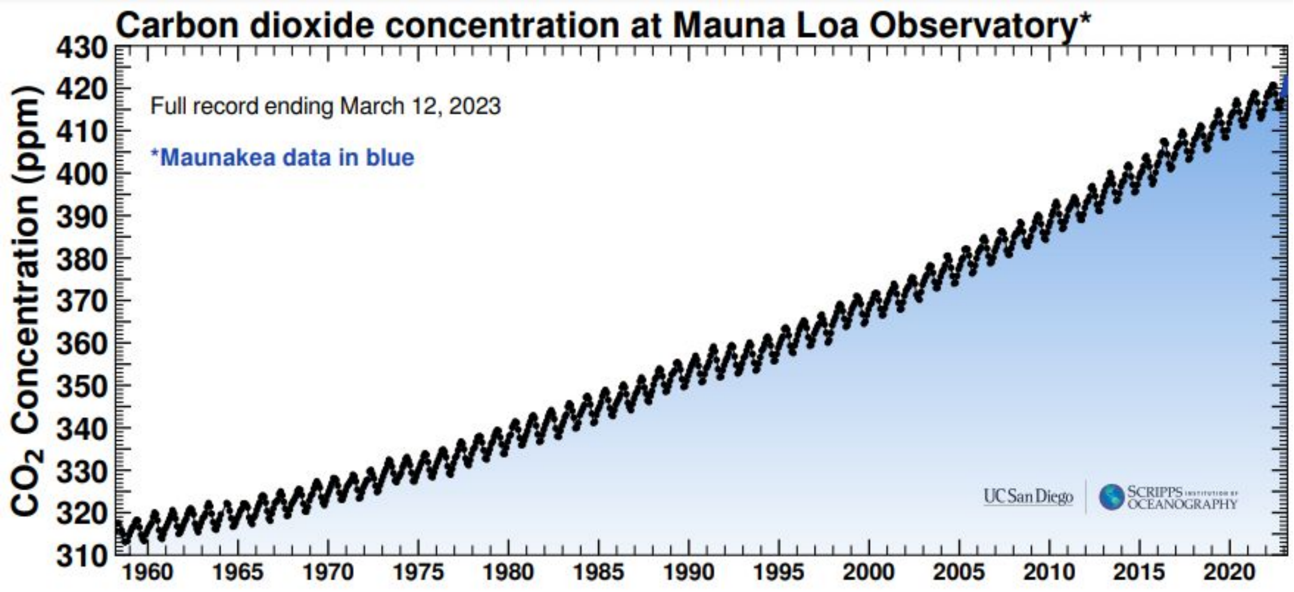
Background

- The ever-increasing energy needs of the industrialized world has continuously raised the concentration of carbon dioxide in the atmosphere from 280 ppm steady state to 418 ppm in 2023 as shown by the adjacent Keeling curve

- Excessive CO_2, the most common greenhouse gas, causes global warming, creating many undesirable effects on earth, including climate change and ocean acidification

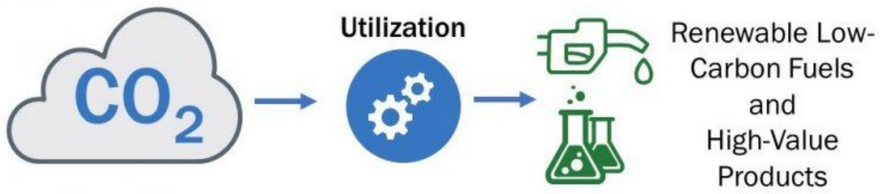
- The global effort to find an innovative technology for conversion of CO_2 hinges on human ingenuity to further technological advances offering high conversion efficiency, scalability, economic viability, and sustainability.

C&E News: Carbon capture's steep climb, 99(26), 28-35, 2021.



CO_2 Capture and Utilization (CCU)

There is an urgent need for mitigation of the global warming effects, by capturing CO_2 from atmosphere and converting into some valuable products.



Chemical and biological approaches can potentially lead to conversion of atmospheric CO_2 to valuable products while contributing to climate change mitigation.

However, the global effort to find an innovative technology for conversion of CO_2 hinges on human ingenuity to further technological advances offering high conversion efficiency, scalability, economic viability, and sustainability.

Zanco et al., *ACS Eng. Au*, 1(1), 50-72. 2021

Chemical and Biological Approaches for CO_2 Conversion

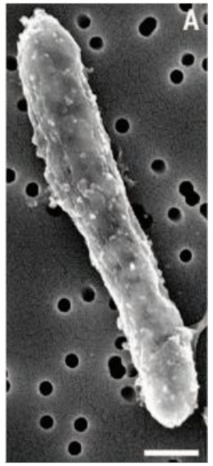
CO_2 conversion processes into value-added chemicals involve two possible approaches: chemical catalysis and biocatalysis.

- ❖ Solid metallic catalysts have dominated chemical catalysis but suffer from low conversion efficiencies and are prone to deactivation by carbonaceous trace contaminants.

  Also, industrial catalyst $Cu/ZnO/Al_2O_3$ and different variations widely tried for CO_2 hydrogenation to CH_3OH require extreme conditions of temperature (150–350 °C) and pressures (30 bar)

- ❖ Biocatalysts utilized in gas fermentation process operate under ambient temperatures and pressure and tolerate contaminants.

  Acetogenic *Clostridium* organisms together with H_2 or CO as reductant, have been used as promising biocatalysts to produce biofuels and chemicals.



M. thermoacetica

CO_2 Conversion – Other Approaches

Recently, Gallium (Ga)-based liquid metals (LM) have shown intriguing properties for catalysis, exhibiting a high reduction potential providing the overall driving force for the CO_2 reduction reaction.

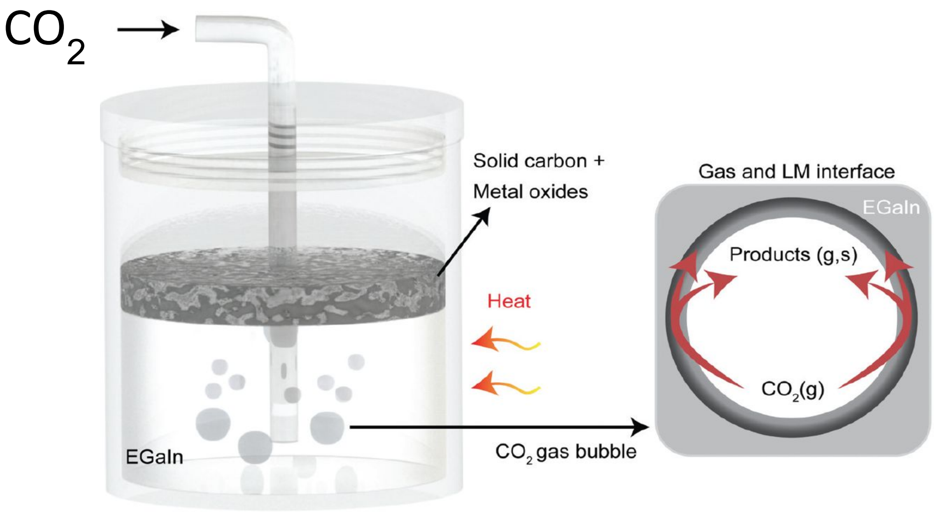
Gallium (Ga) is a silvery-white liquid (much like mercury).

Ga-based LMs can dissolve other metals to form a range of alloys and have been successfully used in methane dehydrogenation producing H_2 and solid carbon.

Zuraiqi et al. (2020), Liquid Metals in Catalysis for Energy Applications, *Joule* 4(11), 2290 – 2321.
Tang J. (2022) , Liquid Metal Enabled Mechanical Energy Induced CO_2 Conversion, *Adv. Mat*, 34, 2105789.

CO_2 Reduction Process to Solid Carbon and O_2

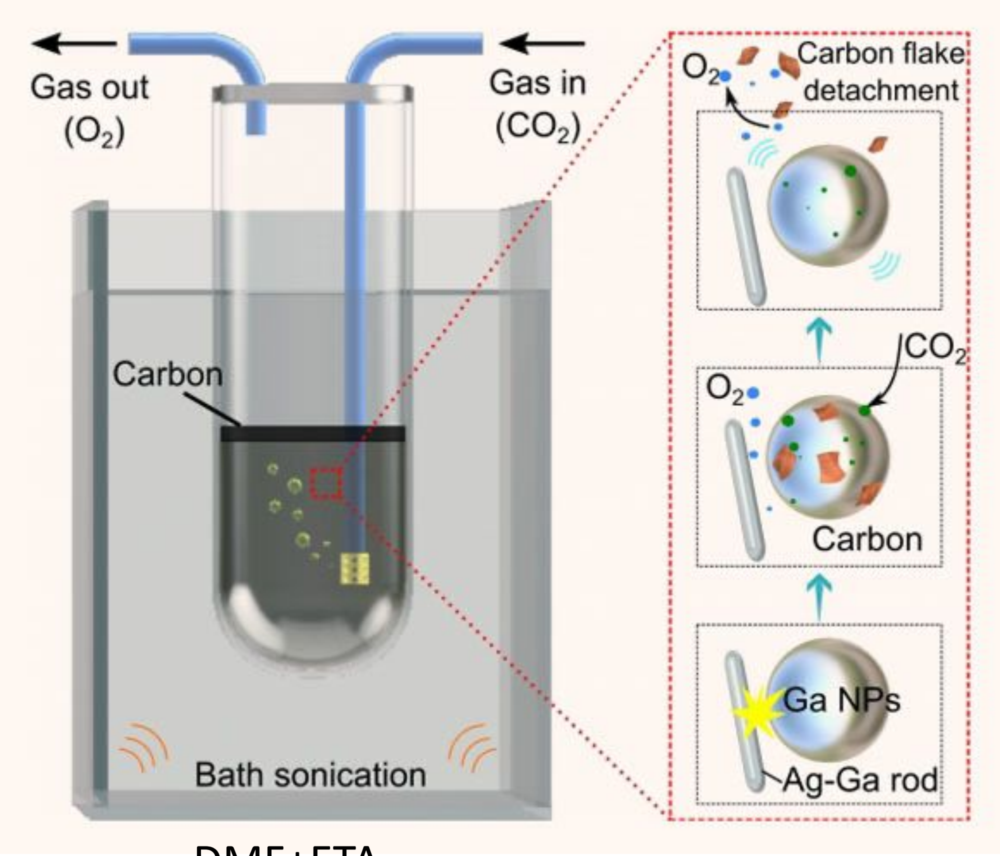
- An Australian process was published in 2022 that uses liquid metals Ga and alloy Ga/AgF at nanometer scales and heated to around 40°C.
- CO_2 gas is bubbled up to the surface of the heated liquid metal to kickstart the chemical reaction.



- The nonpolar nature of the liquid Ga/AgF interface allows the solid carbon flakes to exfoliate, keeping the active sites accessible.

➔ My project is to demonstrate a process to reduce CO_2 to Carbon using this reported process as a starting point

An overview of the CO_2 dissociation process over liquid gallium/AgF



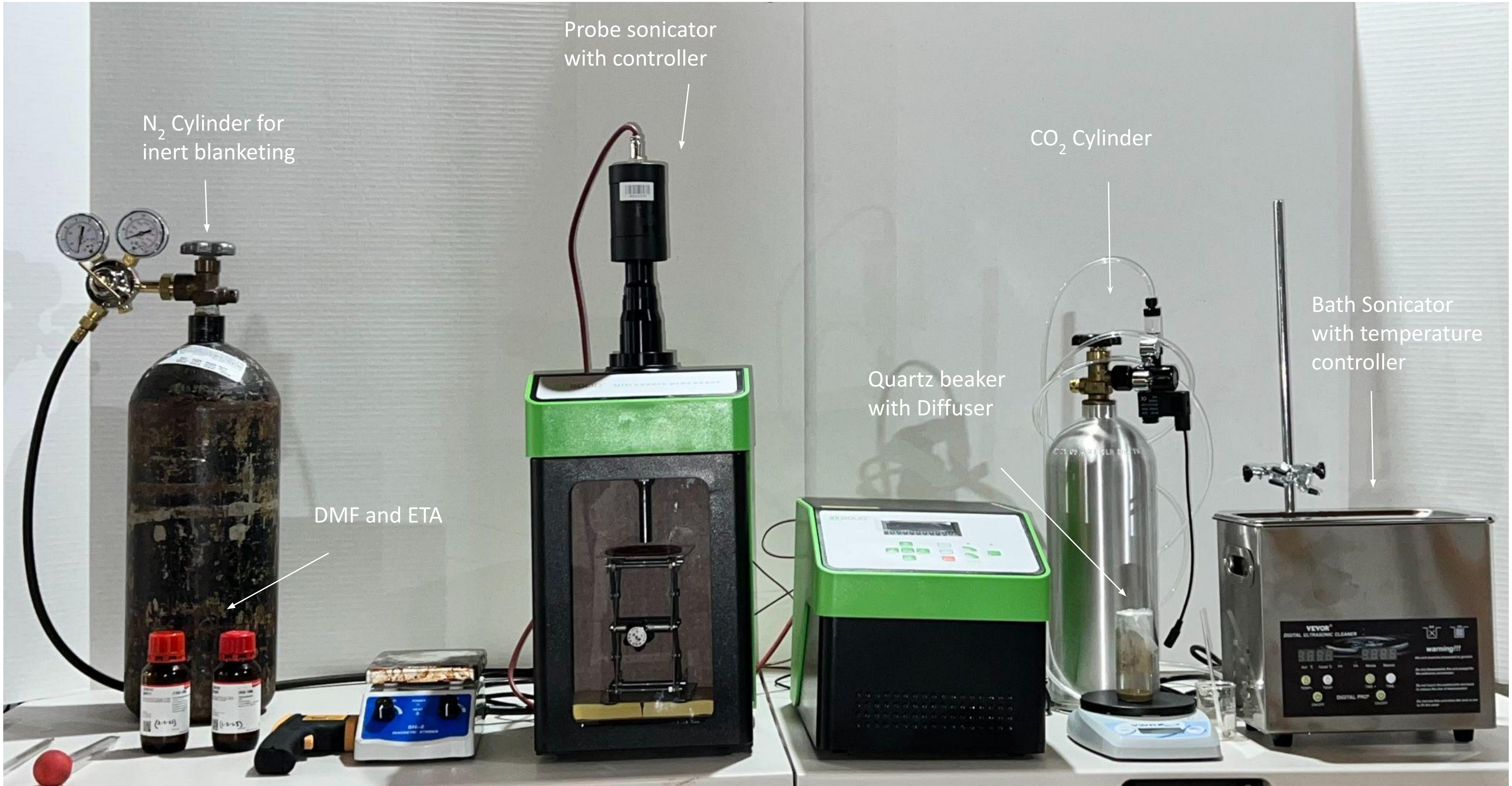
DMF+ETA

Representation of the interaction between gaseous CO_2 and the molten metal to produce solid carbon and the ensuing generation of Ga oxide is shown.

Materials Used in the Experiment

- Gallium (Gallant Metals Store- 99.99%)
- Ag(I)F (Sigma Aldrich 99%)
- Dimethyl Formamide (DMF) (Sigma Aldrich 99.8%, anhydrous)
- Ethanolamine (ETA) or 2-Aminoethanol (Sigma Aldrich 98%)
- 5 lb CO_2 Cylinder with CGA 320 Valve
- CO_2 Regulator with Bubble Counter and Check Valve
- CO_2 Proof Tubing 5/16 inch
- Aquario CO_2 Diffuser
- US Solid Sonicator Ultrasonic Homogenizer Cell Disruptor Mixer, 450W
- Vevor Digital Ultrasonic Bath Sonicator (TH20A)
- Nitrogen 150 psi Gas Regulator
- 40 lb N_2 Cylinder with CGA 580 Valve
- Glass Dropper with Bulb
- Electronic Mass Balance

Experimental Set Up for Liquid Ga/AgF-based CO_2 Reduction to Solid Carbon



Detailed Experimental Protocol

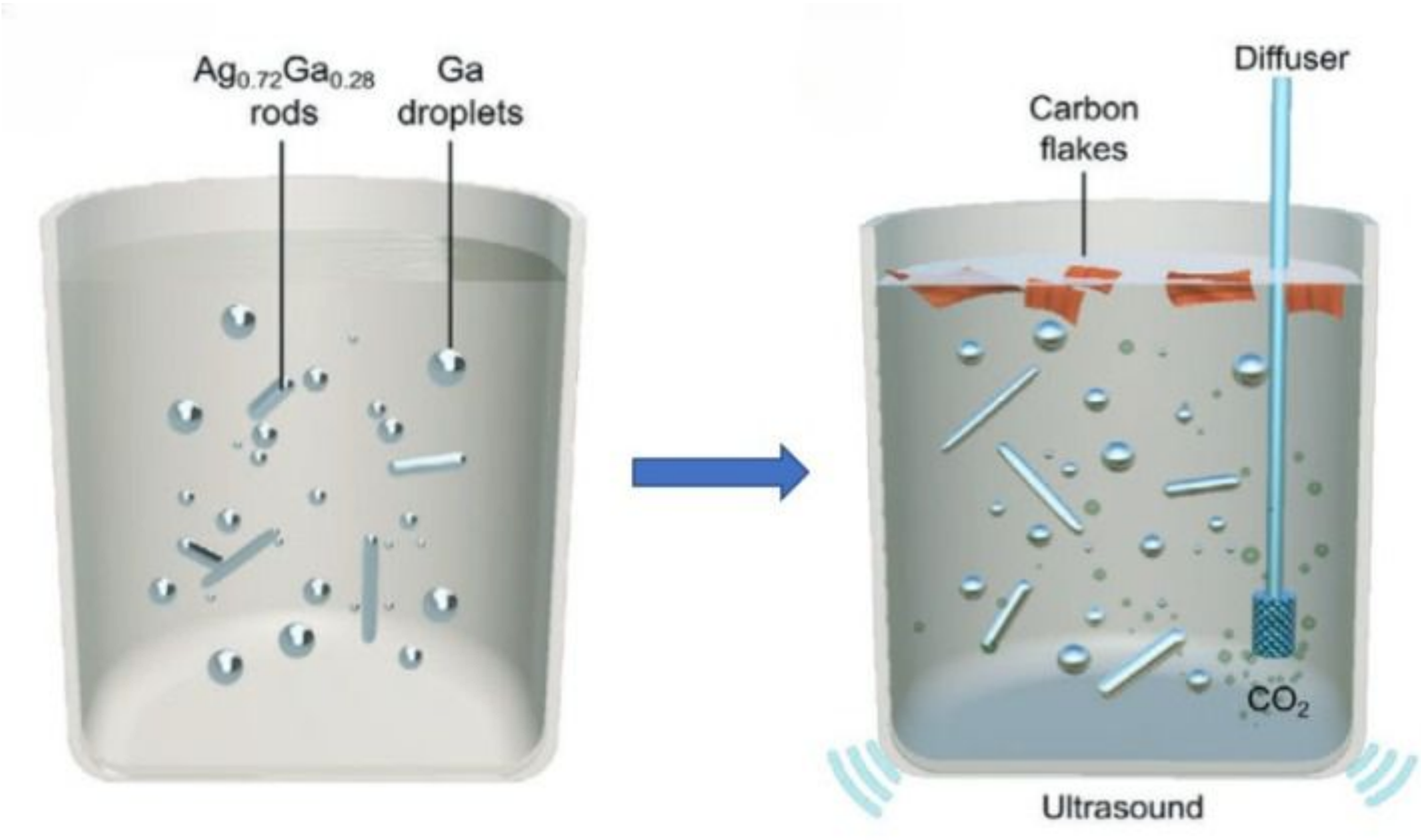
1. Melt Gallium in a quartz tube in 60 ^{o}C water bath
2. Add 5 mL N,N-Dimethylformamide into a Quartz beaker
3. Transfer 7 g liquid Gallium using pipet with beaker on electronic balance
4. Add 2 mL of 1M HCl and 3 mL deionized water
5. Add 1 g Silver(I) Fluoride protecting from light
6. Add 2 mL Ethanolamine, making the total volume approx. 20 mL.
7. Sonicate with a 450 W US Solid Sonicator (90% setting with 9 sec ON and 1 sec OFF) with tip about 1 cm below surface of liquid for 30 minutes in a N_2 blanketed environment.
8. Keep in 40 ^{o}C bath temperature in a Ultrasonic Bath Sonicator with Ultrasonic frequency 40KHz power 120W.
9. Bubble CO_2 through a diffuser at ~80 bubbles/min through water for 5 hours, 30 minutes at a time with 1 minute rest in between.
10. Checked for presence of Carbon through Raman spectroscopy

Experimental Procedure for Ga/AgF-based CO_2 Reduction to Solid Carbon

- Ga and AgF (7:1 mass ratio) were sonicated together using a probe sonicator for 30 min to generate sub-micrometer Ga droplets and $Ag_{0.72}Ga_{0.28}$ rods of micrometer lengths.
- Ga and AgF were mixed in a DMF solution which also contained 0.10 m HCl to remove the native oxide on the surface of Ga.
- In the reactor, CO2 was bubbled into DMF-ETA through a diffuser to facilitate its dissolution.
- The dissolved CO2 was reduced to solid carbonaceous materials at the interface of the Ga droplets.

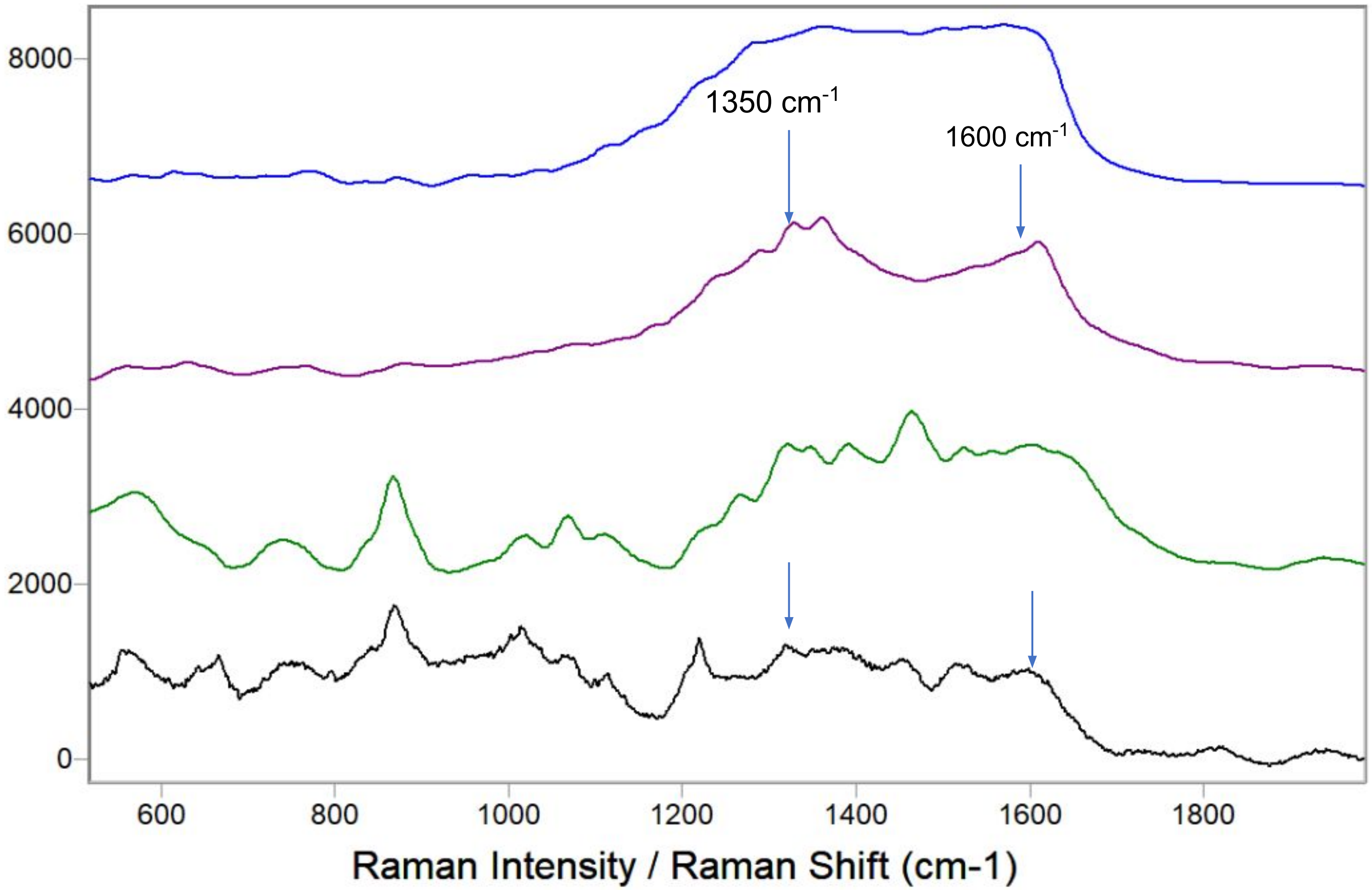
Illustration of the CO_2 Conversion Process

The formation of $Ag_{0.72}Ga_{0.28}$ rods and Ga nano-droplets are found to be crucial for the conversion to proceed



Adapted from Tang J. (2022), Adv. Mat, 34, 2105789; **https://doi.org/10.1002/adma.202105789**

Raman Spectra of Carbonaceous Material post CO_2 Catalytic Reduction in Ga/AgF Liquid Metal in DMF/ETA



Analysis at 4 spots

Adar F. (2022), Use of Raman Spectroscopy to Qualify Carbon Materials, Spectroscopy, 37(6), 11–15,50
https://doi.org/10.56530/spectroscopy.wx3481u2

Courtesy G. Balakrishnan

Future Mechanistic Investigation of the Conversion to CO_2 to Carbon

CO is reportedly detected in the reaction process

I will be investigating

If CO is an intermediate during the catalytic
conversion of CO2 into carbon
or it is simply a byproduct of the reaction

This will be resolved by directly bubbling CO in the Ga/AgF solution

Formation of Carbon flakes will confirm that it is an intermediate in the catalytic conversion of CO2 to carbon

References

- Zuraiqi K. et al., Direct conversion of CO_2 to solid carbon by Ga-based liquid metals. Energy & Environ Sci, 15, 595-600, 2022
- Tang J. et al. Liquid metal-enabled Mechanical energy-induced CO_2 Conversion. Advanced Materials, 34(1), 2105789, 2021
- Esrafilzadeh, D., Zavabeti, A., Jalili, R. et al. Room temperature CO_2 reduction to solid carbon species on liquid metals featuring atomically thin ceria interfaces. Nat Commun 10, 865, 2019