CATALYTIC CARBON CAPTURE: A LOW-COST CLIMATE CHANGE MITIGATION STRATEGY

SHREY KHETAN

Princeton High School

151 Moore St, Princeton, NJ 08540

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ABSTRACT

Climate change has been considered one of the greatest threats to humanity, driven largely by global release of large amounts of carbon dioxide. While emissions reduction is often targeted in mitigation efforts, carbon cycling or sequestration is also necessary to avoid cataclysmic effects. With this goal in mind, this research reports on initial efforts to develop a reusable and scalable carbon capture and utilization mechanism that utilizes a liquid metal gallium, silver fluoride, Dimethylformamide, and Ethanolamine mixture to capture atmospheric carbon dioxide and reduce it to solid carbon that may be harvested for reuse or sequestration. At temperatures about 40℃, as carbon dioxide that was bubbled through the system, carbon was formed and confirmed via Raman spectroscopy. Further experimentation seeks to determine the effectiveness of increasing the concentration of Ga-Ag(I)F to develop a scalable and economically viable process. It is also proposed to explore the mechanism of conversion by bubbling CO, instead of CO_2, to find if it is a reaction intermediate.

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1. INTRODUCTION

Carbon dioxide is ubiquitous in our atmosphere and is vital for maintaining life on our planet. It is an important greenhouse gas that helps to trap heat in our atmosphere. Without it, our planet would be inhospitably cold. However, the ever-increasing emission of anthropogenic CO_2 into our atmosphere is causing average global temperatures to rise, provoking dramatic climate changes. Large amounts of CO_2 emissions are produced by combustion of fossil fuels used in industry and transport and the production of oil and natural gas, reaching around 35 billion metric tons of CO_2 released in 2020. The concentration of atmospheric CO_2 is increasing much faster than Earth can absorb it resulting in global climate change. Mauna Loa Observatory in Hawaii has been measuring changes in atmospheric CO_2 concentration since 1958 and has observed a buildup of CO_2 from about 316 ppm to about 418 ppm in 2023 (Figure 1).

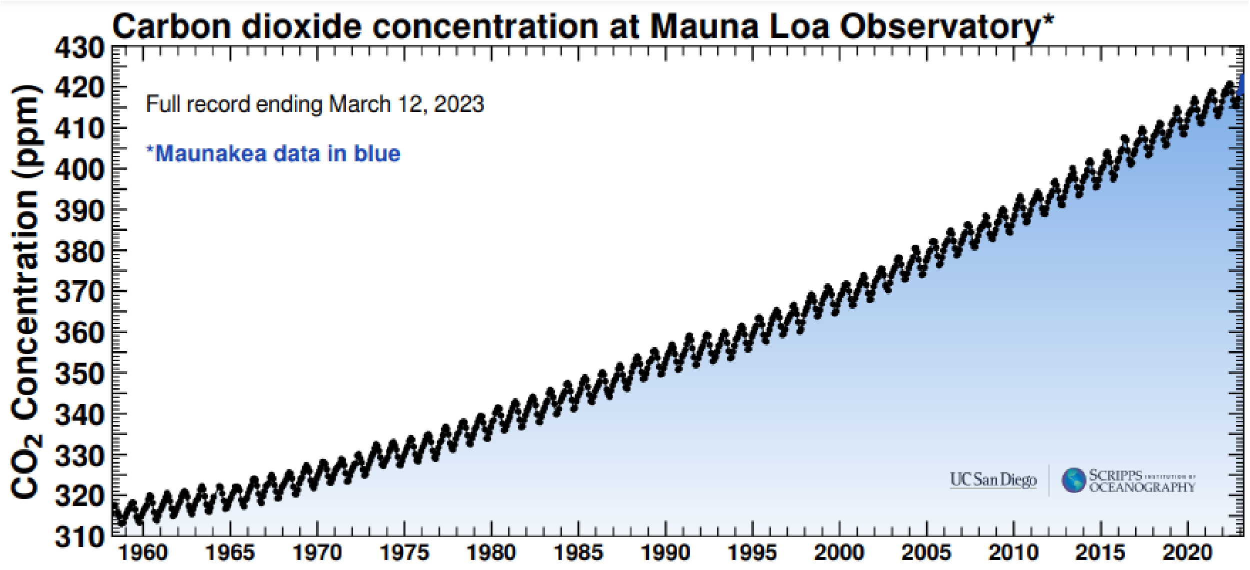

Figure 1. Keeling Curve showinng the accumulation of carbon dioxide in the Earth's atmosphere based on continuous measurements taken on the island of Hawaii from 1958 to the present day

The reason for global warming is simple: incoming light from the sun hits the earth's surface, which absorbs most of that energy, heating the planet. The CO_2 in the atmosphere then absorbs much of that outgoing heat, sending much of it right back to the surface, instead of allowing it to escape earth's atmosphere into space. The gas traps more heat from the sun, making the planet much warmer than it would otherwise be. The process is known as the greenhouse effect (Braga, 2014). When gasses like CO_2 trap excessive amounts of heat in this way, they become dangerous because of all the negative effects they cause to life on Earth. Thus, excessive CO_2 is the most important contributor to human-caused global warming, and the primary source of global climate change. Climate change is evident from increases in global average air and ocean temperatures, declining snow cover and changing precipitation patterns and rising global average sea levels (IPCC, 2007). Climate change is leading to catastrophic events such as melting of glaciers, rapid change in ecosystems, and extreme weather. It also is leading to the major problem of ocean acidification where seawater is becoming rapidly more acidic and already impacting corals and other organisms with shells. These effects can destabilize the climate and severely impact the current way of life and make for an unlivable world.

Rising global temperatures caused by greenhouse warming are interacting differently at different locations and alterations are manifold. It is expected that climate change will accelerate the hydrological cycle with an increasing intensity of rainfalls and frequency of extreme weather events. Climate change threatens communities and sectors across the country, including through floods, drought, extreme heat, wildfires, and hurricanes. There is growing evidence that climate change will alter water availability and water quality. For example, irrigated agriculture, where the largest amounts of water are used worldwide (Schneider, 2013), is particularly sensitive to changes in precipitation, temperature, and carbon dioxide levels. An example of the impact of climate change on water availability is the long-term drought trend that has been seen in California. Smaller snowpack on the mountains is not able to provide water for the rivers throughout the year, especially impacting agriculture. Rising sea levels are bringing more salt water into the deltas which require more freshwater to be pushed into the delta leading to less water available for irrigation ("Climate Change and Water," 2022).

There are two complementary approaches to avoid the adverse impacts of increasing global temperature due to anthropogenic emissions of greenhouse gases - which refers to measures that (i) reduce atmospheric CO_2 concentration by reducing the rate of emissions or (ii) by increasing the rate of removal of atmospheric CO_2. Combating the worst effects of climate change requires the world to go for a multi-pronged approach of technological solutions. Transition of electric power generation to renewable energy sources like solar and wind, and transportation shift to electric vehicles would reduce the further CO_2 emissions and its further accumulation into the atmosphere. Nonetheless, slashing emissions will not be enough. Carbon dioxide removal from the atmosphere is going to be necessary, along with emissions reductions, to prevent the most devastating effects of climate change.

We need gigaton-scale removal of CO_2 from the atmosphere. Carbon capture and storage (CCS) has been proposed to stabilize and possibly reduce overall CO_2 concentration in the atmosphere. For this the gas is pumped into deep underground reservoirs or converted to an inert solid such as limestone. Another promising solution is carbon capture and utilization (CCU) technologies for CO_2 conversion that turn into raw materials or high-value products (Olah et al, 2011). McKinsey & Company estimates that it has the potential to be a trillion-dollar market by 2030 (Roberts, 2019).

There is a critical need to transform CO_2 to useful and high value-added chemicals These transformations need to follow one or a combination of chemical pathways—electrochemical, photochemical, biochemical, or thermochemical—with sufficient efficiency and low infrastructure costs to produce market-competitive chemicals and fuels.

Figure 2. Technologies required for conversion of CO_2 into Carbon fuels and high-value products

Over many decades, the gas-phase reduction of CO_2 has been intensively investigated using a wide range of catalysts and different experimental conditions. A major challenge has been achieving selectivity while simultaneously maintaining a high rate of conversion.

As an energetically low and stable compound, CO_2 does not participate in most chemical reactions or requires external energy for activation. Hence, catalytic systems have been commonly engaged to lower the energy barrier for transformation of CO_2 and derive its conversion into useful compounds. Chemical catalysis and biocatalysis are the two possible practical approaches to convert CO_2 into value-added chemicals.

Among the chemical catalysis approaches, solid heterogeneous transition metal-based catalysts have dominated and rely on the expenditure of hydrogen as a reducing agent and need an external energy input to thermally derive the reduction process. These processes suffer from low conversion efficiencies and are prone to deactivation by carbonaceous trace contaminants. For example, Fischer Tropsch process using industrial copper-based catalyst $Cu/ZnO/Al_2O_3$, can convert syngas (a mixture of CO and H_2) into methanol (CH_3OH). However, these reactions require extreme conditions of temperature (150–350 °C) and pressures (40 bar). It is evident that further catalyst development is required, particularly those that exhibit high activity at mild operating conditions (i.e <200 ºC) for the selective conversion.

The other approach using biocatalysts is utilized in the gas fermentation process, operating under mild temperature (30–37 ºC) and atmospheric pressure. For example, Acetogenic *Clostridium* bacteria combined with H_2 or CO as reductant, have a proven ability to produce biofuels and chemicals. An Illinois-based company LanzaTech uses bioreactors filled with *Clostridium autoethanogenum* bacteria to ferment industrial CO_2, CO, and renewable hydrogen from electricity into ethanol (C_2H_5OH). This kind of bioconversion can handle messy waste-gas streams, such as those from municipal waste gasifiers, better than chemical processes do. However, there are limitations to biomass concentration and growth rate and the process poses challenges along with promise (Bae et al., 2022).

Other alternative strategies focused on photo-catalytic or electro-catalytic reduction routes remain hinged on further technological advances. The global effort to find an innovative technology for conversion of CO_2 requires high conversion efficiency, scalability, economic viability, and sustainability.

A recent process made it possible for conversion of gaseous CO_2 into solid carbon and pure oxygen at near room temperature using a Group 13 metal liquid Gallium (Ga) catalyst. The technology potentially could remove CO_2 out of the air and permanently store it in a solid form. Gallium (Ga) is a silvery metal soft enough at room temperature to be cut with a knife. It melts at 30 °C, and liquid Ga looks silvery-white much like mercury. Ga has low toxicity, low bulk viscosity, near zero vapor pressure, and is an excellent electrical conductor. It has excellent catalytic activity that can be enhanced by dissolving other metals to form a range of alloys. It can economically capture and convert substantial quantities of greenhouse gases such as CO_2. Ga-based liquid metals (LM) have shown unique properties for catalysis, exhibiting a high reduction potential providing the overall driving force for the reduction of CO_2 (Kalantar-Zadeh et al., 2021).

Figure 3. Liquid Gallium metal

The use of Ga-based liquid metals as the working fluid has been based upon a careful selection process along several criteria to sustainably convert substantial quantities of greenhouse gases such as CO_2: economically viability, inertness towards the reaction gases, high thermal conductivity, high density compared to carbon, nontoxicity, and long-term chemical stability.

A research group in Australia has developed a new technique that offers CO_2 reduction into carbon. This is a promising strategy to reduce the atmospheric CO_2 concentration and produce a value-added product at the same time (Tang, 2022). The reaction environment is at ambient pressure. Using liquid metals as a catalyst, it has been shown that CO_2 gas can be converted into carbon even at near room temperature, in a process that's efficient and scalable.

For this science project, I have developed a simplified bench-top experiment taking cues from the Australian process for reduction of CO_2 into solid carbon that maintained the basic concept at a minimal budget.

2. MATERIALS AND METHODS

A list of the equipment and materials procured is given as under:

- Gallium (99.99% Purity)
- Ag(I)F (99%)
- DMF (99.8%, anhydrous)
- Ethanolamine (ETA) or 2-Aminoethanol (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
- Ultrasonic Homogenizer Sonicator Cell Disruptor Mixer, 450W
- Ultrasonic bath sonicator
- Nitrogen 150 psi Gas Regulator
- 20 lb N_2 Cylinder with CGA 580 Valve
- Glass Dropper with Bulb
- Quartz beaker

EXPERIMENTAL PROCEDURE:

This research aims to synthesize sub-micrometer Gallium droplets and micrometer length Ag/Ga rods through sonication in a DMF solution containing HCl and Silver(I) Fluoride. The synthesis process involved several steps as follows.

To generate sub-micrometer Gallium droplets and micrometer length Ag/Ga rods, Gallium and Silver(I) Fluoride were used in a mass ratio of 7:1. Liquid Gallium was melted in a quartz tube using a 60℃ water bath. A quartz beaker containing 5 mL of N,N-Dimethylformamide was placed on an electronic balance and 7 g of Gallium was added using a pipette. Subsequently, 2 mL of 1M HCl and 3 mL of deionized water were added to the mixture along with 1 g of Silver(I) Fluoride. 2 mL of Ethanolamine was also added, to make the total volume approximately 20 mL. The mixture was then sonicated for 30 minutes using a probe sonicator in a closed container at 400W setting with 9 sec on and 1 sec off, with the tip approximately 1 cm below the surface of the liquid in a N_2-blanketed environment (Figure 4).

CO_2 was bubbled through a diffuser at approximately 80 bubbles/min into DMF-ETA mixture to facilitate its dissolution, and the dissolved CO_2 was reduced to carbonaceous materials at the interface of the Gallium droplets. The beaker was then kept in a 40 deg C Ultrasonic Bath Sonicator with Ultrasonic frequency 40KHz and power 120W. CO_2 was bubbled for 5 hours, with 30-minute intervals and 1-minute rests in between.

Finally, the mixture was checked for the presence of carbon using Raman spectroscopy.

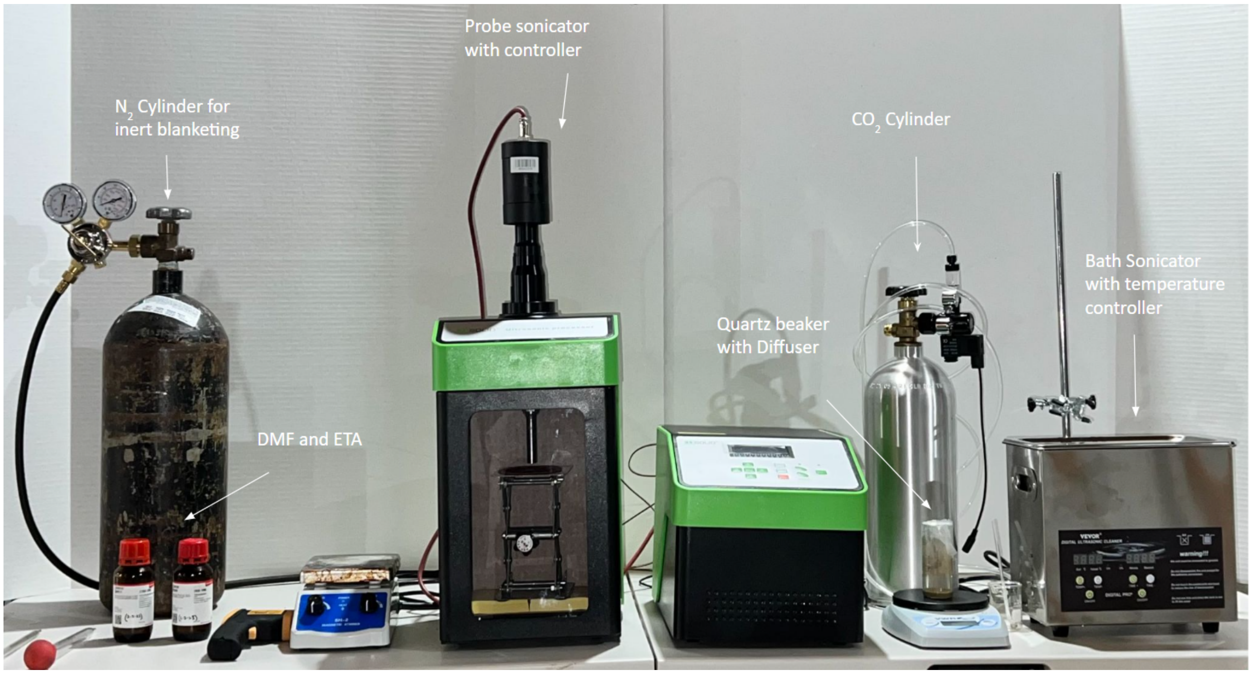

Figure 4. A experimental set-up consisting of a N_2 Cylinder, Probe sonicator, Quartz beaker with diffuser, CO_2 cylinder with aquarium regulator, and an ultrasonic bath sonicator

3. RESULTS AND DISCUSSION

A Raman spectra of the carbonaceous material taken after post CO_2 catalytic reduction at 4 separate spots indicated two peaks at 1350 cm^{-1} and 1600 cm^{-1} confirming presence of carbon in the experiment (Figure 5).

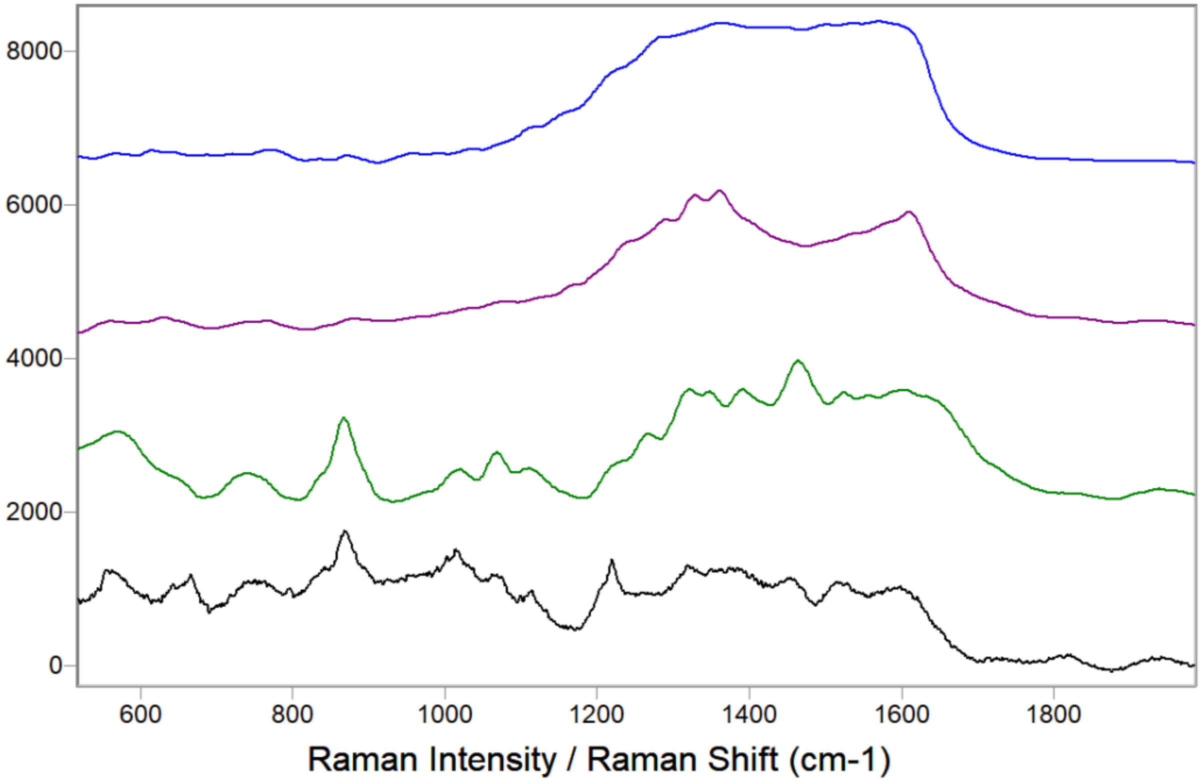

Figure 5. Raman Spectra collected using Horiba Scientific Raman Microscope of Carbonaceous Material post CO_2 Catalytic Reduction in Ga/AgF Liquid Metal in DMF/ETA. The presence of carbon is shown by peaks at 1350 cm-1 and 1600 cm-1. (Courtesy: G. Balakrishnan)

Utilization of a sustainable system to regenerate gallium for CO_2 reduction to carbon: The formation of solid carbon and oxygen on reduction of CO_2 on contact with gallium liquid metal can be accompanied with concurrent oxidation of gallium forming gallium oxide. It has been reported that coupling with silver(I) fluoride in the reaction medium reduces gallium oxide reverting it back to gallium. A sustainable Gallium-based process that has built-in reduction of gallium oxide back to gallium, could make a perpetual machine for production of carbon and oxygen. This project aimed to establish that this is feasible.

Initially a handheld sonicator of lower power of about 250W was used to develop the nanoparticle dispersion and a magnetic stirrer was used for keeping the particles from coalescing while bubbling CO_2. However, this did not result in carbon formation. Subsequently, a higher power probe sonicator with a insulted contained box was used and also a bath sonicator was used to keep gallium and silver fluoride in suspension while bubbling CO_2. This enhanced setup was also not successful, in producing carbon. Finally, upon realizing that N_2 inert atmosphere is critical while using a sonicator this was implemented and led to successful detection of carbon.

In further experiments it would be desirable to investigate dependencies of operating parameters to improve the process efficiency including Gallium-silver fluoride concentrations, bubble residence times, bubble size, potential carbon sediment locations etc. Future tests can be conducted with higher concentrations of the Gallium:Silver Fluoride combination to determine if the carbon dioxide reduction to carbon is enhanced. To identify potential optimizations, reactor geometry, inlet types and the heating system could be varied. Especially the aspect of multi-inlets as well as the effect of electromagnetic stirring with regards to increase of carbon yield can be a focus. In addition, the use of carbon monoxide can be tested to determine if it is an mechanistic intermediate in the conversion of carbon dioxide to carbon.

The nanoparticle process for reduction of CO_2 to solid Carbon and Oxygen could have potential application for generating needed oxygen on Planet Mars. Martian atmosphere is made up of 96% CO_2 and just about 0.13% of O_2 as compared to 21% O_2 in the earth's atmosphere. The inhospitable environment of Mars needs a minimum of breathable Oxygen to make it inhabitable. A direct conversion of CO_2 to O_2 may help solve some of the challenges, such as creating a breathable environment for future outpost there. NASA is experimenting with electrolysis of Martian soil rich in perchlorate to produce needed oxygen and the nanoparticle process could be useful as an alternative approach.

4. CONCLUSIONS

Feasibility of CO_2 catalytic conversion to carbon based on liquid Gallium metal nano-particle technology was successfully demonstrated. While more research needs to be done to understand the underlying mechanism and to optimize for economically viable scaleup, this is an important first step to delivering cost-effective sustainable catalytic conversion of carbon dioxide.

5. ACKNOWLEDGEMENTS

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