Environment and Natural Resources Trust Fund

2022 Request for Proposal

General Information

Proposal ID: 2022-092

Proposal Title: Reducing greenhouse gases through CO2 conversion to ethanol

Project Manager Information

Name: Sam Toan

Organization: U of MN - Duluth

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Project Basic Information

Project Summary: To mitigate greenhouse gas emissions in Minnesota, we propose CO2 capture and conversion to ethanol with nano-fluids as the sorbent and electrolyte, enhanced by a non-noble metal single-atom three-dimensional graphene electrocatalyst.

Funds Requested: $400,000

Proposed Project Completion: June 30 2024

LCCMR Funding Category: Air Quality, Climate Change, and Renewable Energy (E)

Project Location

What is the best scale for describing where your work will take place?

Region(s): NE

What is the best scale to describe the area impacted by your work?

Statewide

When will the work impact occur?

In the Future

Narrative

Describe the opportunity or problem your proposal seeks to address. Include any relevant background information.

The large-scale utilization of unsustainable fossil fuels has led to the global energy crisis and continuously increases the atmosphere's carbon dioxide (CO_2) concentration. Affected by greenhouse gas (GHG) emissions, Minnesota's climate has changed significantly in recent years. Under the current demand for CO_2 reduction, the conversion of CO_2 from air into high value-added ethanol products is of great significance to Minnesota.

Direct CO_2 capture and conversion to ethanol requires solving three problems: 1) How to effectively capture CO_2, 2) How to efficiently activate inert CO_2 molecules, and 3) How to reduce costs to facilitate commercial implementation. Synergistic effects of nano-fluids and a three-dimensional graphene-supported non-noble metal single-atom electrocatalyst may potentially become a game-changer in the field of CO_2 capture and conversion due to its promising performance, including 1) Greatly improved reaction kinetics, 2) Increased surface contact area of molecules, leading to enhancement of mass and energy transfer rates, 3) Greatly decreased net energy consumption, possibly down to zero, 4) Enhanced CO_2 capture and conversion efficiency, and 5) Improved selectivity and efficiency of electrocatalytic CO_2 reduction through nano-restriction strategies.

What is your proposed solution to the problem or opportunity discussed above? i.e. What are you seeking funding to do? You will be asked to expand on this in Activities and Milestones.

The chemical properties of CO_2 are relatively stable; however, the electrocatalytic reduction of CO_2 still has problems, such as low current efficiency, poor product selectivity, and high reduction overpotential. This project intends to research electrolyte and catalytic materials to effectively capture and utilize CO_2 from the air.

Nano-fluids are attractive because of their excellent electrochemical properties and high solubility for CO_2. Some ionic liquid nano-fluids even help catalyze the electrocatalytic reduction of CO_2. In this project, the aqueous or ionic liquid nano-fluid will be the electrolyte for the electrocatalytic reduction of CO_2 to minimize the impact of CO_2 diffusion on the reaction. The nano-fluid will also serve as the source of hydrogen to realize the hydrogenation reduction reaction of CO_2.

We plan to support copper (Cu) single-atom catalysts on the three-dimensional graphene (3DG) framework. A large number of experiments have shown that metallic Cu is beneficial to the formation of ethanol. The carbon skeleton of 3DG has a large specific surface area that can fully adsorb CO_2, and 3DG with abundant edge sites exhibits good CO_2 electrocatalytic activity and high selectivity.

What are the specific project outcomes as they relate to the public purpose of protection, conservation, preservation, and enhancement of the state's natural resources?

As a clean energy, ethanol is considered to be one of the best replacements for fossil fuels. Minnesota is one of the pioneering states in the United States to promote the application of E10, E15, and E85 ethanol-gasoline blends and has successfully used it for more than 40 years. Removal of CO_2 from industrial sources or the atmosphere, together with cutbacks in fossil fuel use, effectively relieves the dual pressures on Minnesota's environment and resources.

Activities and Milestones

Activity 1: Construct a two-component catalyst with a single copper (Cu) atom supported by a three-dimensional graphene (3DG) framework.

Activity Budget: $132,778

Activity Description:
Since the linear CO_2 molecule is fully oxidized and highly stable, efficient and robust electrocatalysts need to be designed and prepared to promote this kinetically slow reduction process. The catalytic conversion of CO_2 to value-added ethanol is considered one of the most promising approaches that can reduce the concentration of CO_2 in the atmosphere and achieve a sustainable and carbon-neutral cycle. Although precious metals, such as silver and gold, exhibit superior CO_2 reduction selectivity, they are not suitable for practical application because of their scarcity, high cost, and questionable stability. Due to their high active site density, single-atom catalysts generally show better activity than conventional catalysts. 3DG has a controllable pore structure, high specific surface area, and excellent conductivity, making it an ideal framework monomer. The non-noble metal single Cu atoms will be highly dispersed on the 3DG framework to obtain a single-atom electrocatalyst for CO_2 conversion with high activity and high conductivity. Through in-situ analysis techniques and theoretical calculations, the mechanism of the electrocatalytic reduction of CO_2 to ethanol by the new catalyst system will be explored.

Activity Milestones:

Description	Completion Date
Prepare 3DG-supported monoatomic copper two-component catalyst.	December 31 2022
Evaluate the electrocatalytic effect of the catalyst.	June 30 2023
Use in-situ infrared, in-situ Raman, and theoretical calculations to analyze the CO_2 electrocatalytic reduction mechanism.	December 31 2023

Activity 2: Design aqueous or ionic liquid-based nano-fluids for sorbent and electrolyte to enhance CO_2 capture from air and conversion to ethanol.

Activity Budget: $132,777

Activity Description:
Solid−liquid interface engineering is a promising strategy to go beyond designing the catalyst's structure toward a complete optimization of the electrocatalytic reaction environment. In particular, nano-fluid (aqueous or ionic liquids) electrolytes have been established as efficient media for the electrocatalytic reduction of CO_2(CO_2RR). Nano-fluids have relatively high CO_2 solubility and can also activate CO_2, facilitate CO_2 transfer, and stabilize the charged CO_2 intermediates, such as CO_2.- at the catalyst surface, thus serving as a "co-catalyst" for CO_2RR. The influence of aqueous or ionic liquid nano-fluids and the proportion of water on the absorption of CO_2 and the electrochemical reduction will be investigated

Activity Milestones:

Description	Completion Date
Determine the CO_2 absorption effect of aqueous nano-fluids and its influence on the electrocatalytic reduction of CO_2.	March 31 2023
Determine the CO_2 absorption effect of ionic liquid nano-fluids and its influence on the electrocatalytic reduction of CO_2.	June 30 2023
Summarize the structure-activity relationship of catalyst and electrolyte from the analysis (activity 2 and 5) and the mechanism discussion (activity 4) results.	June 30 2024

Activity 3: Conduct a preliminary life cycle assessment (LCA) of the new CO_2 capture system to determine potential environmental impacts.

Activity Budget: $27,336

Activity Description:

A preliminary life cycle assessment (LCA) will be conducted to determine the potential life cycle environmental impacts of the new CO_2 capture system. The LCA will follow International Organization for Standardization (ISO) guidelines for the overall LCA framework. The system boundary will be established around a representative functional unit (e.g., mass of CO_2 captured). We will then establish an inventory of all material flows, emissions, and resource consumption and describe, characterize, and aggregate these elementary flows for different environmental aspects. Primary life cycle inventory (LCI) data will be collected from the laboratory-scale CO_2 capture experiments. Secondary data will be collected as necessary from peer-reviewed literature, subject matter experts, and established LCI databases, including DATASMART and Ecoinvent v3.6. The LCA will be modeled using SimaPro v9.1.1 software. Environmental impacts will be assessed using the LTS Method, which translates the LCI data into environmental impacts in Human Health, Ecosystems, Resources, Cumulative Energy Demand, Climate Change (100-year time horizon), and Water Use impact categories. Ultimately, this LCA will identify environmental "hot spots" to guide the future pilot-scale development and demonstration of the technology.

Activity Milestones:

Description	Completion Date
Complete life cycle inventory of CO_2 capture process.	September 30 2023
Build LCA model of the CO_2 capture process.	March 31 2024
Conduct a life cycle impact assessment to determine potential environmental impacts of the CO_2 capture process.	June 30 2024

Activity 4: Develop models of the catalytic reaction mechanisms and simulations of the CO_2 capture process for analysis and optimization.

Activity Budget: $69,902

Activity Description:

The mechanisms and kinetics for CO_2 absorption reaction will be analyzed and modeled for optimization and incorporation into models of the proposed direct CO_2 capture process. The mechanistic and kinetic models will guide the research activity investigating critical parameters and reaction conditions. The overall CO_2 capture and purification process will be simulated in the Aspen Plus chemical process simulator with models for fluid- and solid-phase interactions with the aim of economic analysis, scale-up for implementation on a demonstration scale, and process analysis and optimization for determining critical operating conditions to minimize cost and energy requirements and maximize the efficiency of CO_2 conversion to ethanol. Process simulations will also guide integration of the technology with existing processes for ethanol production and purification.

Activity Milestones:

Description	Completion Date
Develop models of absorption mechanisms and kinetics	September 30 2023
Simulate the CO_2 capture technology	March 31 2024
Analyze and optimize the CO_2 capture process	June 30 2024

Activity 5: Physicochemical analysis of novel CO2 capture and conversion process via operando Raman spectroscopy.

Activity Budget: $37,207

Activity Description:

Operando Raman spectroscopy will be carried out to understand this novel electrocatalytic reduction of CO2. Interface reactions occurring on the surfaces of Cu-3DG during CO2 reduction will be studied. Intermediate species, as well as Cu and oxygen associated vibrational modes, will be monitored during the reduction. Based on the Raman data, and along with other physical characterizations, we aim to understand the kinetics and electrochemistry of CO2RR.

Activity Milestones:

Description	Completion Date
Design and produce the necessary components and set-up operando Raman.	June 30 2023
Carry out operando Raman along with other physical characterizations, such as SIMS and electrochemical measurements.	December 31 2023
Summarize interfacial reaction results and discuss the mechanism.	March 31 2024

Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
Richard Davis	University of Minnesota Duluth	Co-PI	Yes
Anna Lee	University of Minnesota Duluth	Co-PI	Yes
Matthew Aro	University of Minnesota Duluth	Co-PI	Yes

Long-Term Implementation and Funding

Describe how the results will be implemented and how any ongoing effort will be funded. If not already addressed as part of the project, how will findings, results, and products developed be implemented after project completion? If additional work is needed, how will this be funded?

The work related to the production of ethanol by the catalytic hydrogenation of CO2 has received worldwide attention, and it is an effective way to relieve the dual pressures on the environment and resources in Minnesota. If the proposed work is successful, we believe that to advance the technology to commercialization, our work can receive strong financial support from governmental agencies (such as the U.S. Department of Energy) and commercial enterprises. The proposed project also has gained support from collaborators, including Dr. Richard Davis, Dr. Anna Lee, and Mr. Matthew Aro from UMD.

Project Manager and Organization Qualifications

Project Manager Name: Sam Toan

Job Title: Assistant Professor

Provide description of the project manager's qualifications to manage the proposed project.

Dr. Sam Toan, Principal Investigator (PI), is an Assistant Professor of Chemical Engineering at UMD. He has a strong background in materials chemistry, electrochemistry, chemical process, and catalysis studies, particularly in CO2 capture and conversion catalysis work. His work has been published in more than 20 high-quality journals such as Nano Energy and Nature Communications. In addition, he developed several complex chemical process systems to capture CO2 from variety concentration feedstocks, and convert biomass/CO2 to fuel/syngas and various value-added chemical products.

Organization: U of MN - Duluth

Organization Description:

The University of Minnesota Duluth (UMD) is a public, comprehensive regional university that is part of the University of Minnesota System. Offering 16 bachelor's degrees in 87 majors and graduate programs in 24 fields, UMD faculty, staff, and students work together to produce high-quality research that benefits people in Minnesota and beyond. The main research areas targeted by UMD and its Natural Resources Research Institute (NRRI) include ecology and natural resource management, renewable energy, advanced materials and chemistry, minerals and metallurgy, and bioeconomy development. UMD and NRRI collaborate broadly across the University system, the state and the region to address the challenges of a natural resource-based economy. By partnering with industry, business leaders, agency decision-makers and many others, UMD and NRRI researchers frame and deliver on real-world solutions. In the proposed research, the team will access UMD's chemistry and chemical engineering research expertise in CO2 capture and characterization, advanced analytical equipment in UMD's Research Instrumentation Laboratory, and NRRI's expertise and software for life cycle assessment (LCA) modeling.

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineligible	% Benefits	# FTE	Classified Staff?	$ Amount
Personnel								
Sam Toan		PI			26.7%	0.16		$26,130
Richard Davis		Co-PI			26.7%	0.16		$42,647
Anna Lee		Co-PI			26.7%	0.16		$23,515
Matthew Aro		Co-PI			26.7%	0.24		$24,768
Postdoc		Postdoc			20.2%	2		$135,031
Graduate Student		Graduate Student			16.6%	0.5		$27,255
Graduate Student		Graduate Student			16.6%	0.5		$27,255
Undergraduate RA		Undergraduate RA			0%	2		$53,754
							Sub Total	**$360,355**
Contracts and Services								
							Sub Total	-
Equipment, Tools, and Supplies								
	Tools and Supplies	Lab supplies and Chemicals	consumable lab supplies and chemicals will be used to operate the proposed project					$29,077
	Tools and Supplies	Life Cycle Analysis software fee	The license is needed to work on the LCA task					$2,568
							Sub Total	**$31,645**
Capital Expenditures								
							Sub Total	-
Acquisitions and Stewardship								

							Sub Total	**-**
Travel In Minnesota								
							Sub Total	**-**
Travel Outside Minnesota								
							Sub Total	**-**
Printing and Publication								
							Sub Total	**-**
Other Expenses								
		Lab/Scientific Services	Material characterization fees					$8,000
							Sub Total	**$8,000**
							Grand Total	**$400,000**

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request

Non ENRTF Funds

Category	Specific Source	Use	Status	Amount
State				
			State Sub Total	**-**
Non-State				
In-Kind	University of Minnesota	Unrecovered indirect costs at 55% of project costs.	Secured	$220,000
			Non State Sub Total	**$220,000**
			Funds Total	**$220,000**

Attachments

Required Attachments

Visual Component

File: a05d312b-305.pdf

Alternate Text for Visual Component

CO2 emissions from industrial sources and transport vehicles in Minnesota will be efficiently captured and converted to ethanol and other useful products to help Minnesota reach its greenhouse gas emission (GHG) targets and reduce GHG's negative impacts on the climate....

Optional Attachments

Support Letter or Other

Title	File
LCCMR Transmittal letter Toan	4e315ec8-efe.pdf
UMD letter of support_minnesota power	5385d903-ff6.pdf

Administrative Use

Does your project include restoration or acquisition of land rights?

No

Does your project have potential for royalties, copyrights, patents, or sale of products and assets?

Yes

Do you understand and acknowledge IP and revenue-return and sharing requirements in 116P.10?

Yes

Do you wish to request reinvestment of any revenues into your project instead of returning revenue to the ENRTF?

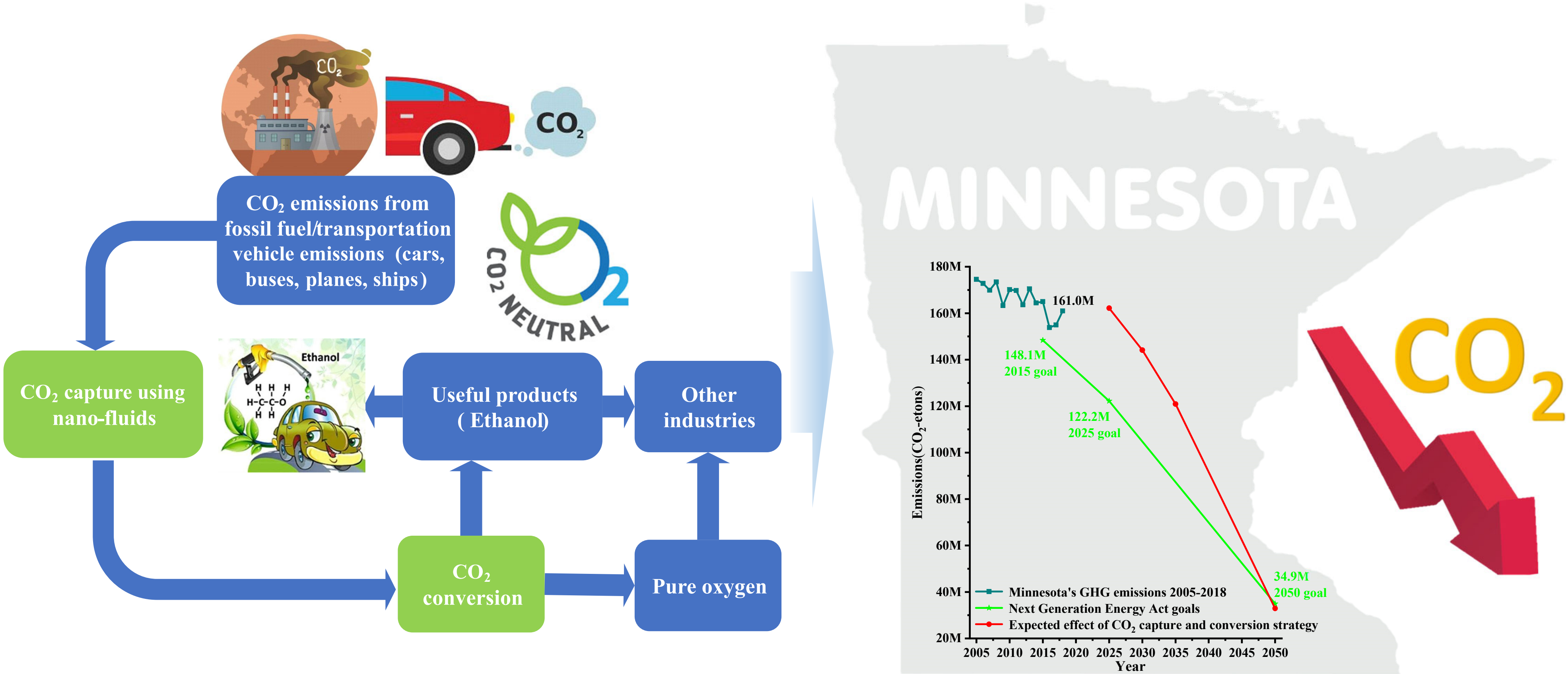
No

Does your project include original, hypothesis-driven research?

Yes

Does the organization have a fiscal agent for this project?

No



CO2
CO2
CO2 emissions from fossil fuel/transportation vehicle emissions (cars, buses, planes, ships)
CO2 NEUTRAL
Ethanol
CO2 capture using nano-fluids
Useful products (Ethanol)
Other industries
CO2 conversion
Pure oxygen
MINNESOTA
CO2
180M
160M
140M
120M
100M
80M
60M
40M
20M
Emissions(CO2-etons)
161.0M
148.1M
2015 goal
122.2M
2025 goal
34.9M
2050 goal
Minnesota's GHG emissions 2005-2018
Next Generation Energy Act goals
Expected effect of CO2 capture and conversion strategy
2005 2010 2015 2020 2025 2030 2035 2040 2045 2050
Year