



Environment and Natural Resources Trust Fund

2024 Request for Proposal

General Information

Proposal ID: 2024-156

Proposal Title: Post-Combustion Capture & Green-Fuel Production via CO2 Reduction

Project Manager Information

Name: Sam Toan

Organization: U of MN - Duluth

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Project Basic Information

Project Summary: To mitigate greenhouse gas (GHG) emissions in Minnesota, we propose to convert post-combustion CO2 to green butanol fuel via a novel CuP2/3D graphene catalyst

Funds Requested: \$200,000

Proposed Project Completion: June 30, 2026

LCCMR Funding Category: Small Projects (H)

Secondary 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.

Power generation from fossil fuels remains the most reliable method for electricity generation, making up more than 80% of the global energy supply. However, fossil fuel combustion generates over 25% of CO₂ emissions. The unsustainable utilization of fossil fuels has led to a global energy crisis and increasing atmospheric CO₂, which breaks the natural carbon cycle and exacerbates the climate crisis. Accordingly, capturing, storing, and utilizing CO₂ is attracting tremendous attention. Flue gas treatments that capture and convert CO₂ emissions to green fuels, like butanol, are vital in addressing the climate crisis while meeting future energy demands.

CO₂ is an ideal feedstock to achieve green fuel production goals since it is a high-volume greenhouse gas (GHG).

Electrochemical CO₂ reduction processes convert CO₂ into value-added products and green fuels. Although precious metals, such as silver and gold, exhibit superior CO₂ reduction selectivity, they are unsuitable for CO₂ conversion to green fuels because of their high cost and questionable stability. Therefore, designing low-cost, stable electrocatalysts for CO₂ reduction is crucial to enabling efficient production of green butanol from CO₂.

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

Unstable homogeneous catalysts for hydrogenating CO₂ to butanol require harsh conditions. Consequently, developing heterogeneous catalysts for CO₂ conversion is challenging. We propose to control the structure of 3D graphene (3DG) electrodes and build a copper diphosphide (CuP₂) nanocluster/3DG composite material, where the 3DG spatial network limits the growth of Cu nanoparticles and prevents aggregation. This project will reveal the relationship between the microstructure and the electrocatalytic performance of CuP₂/3DG composites and clarify the design principles of new composite electrode materials to achieve efficient activation and selective catalytic conversion of CO₂ to butanol under mild conditions. The results will provide a scientific basis for the efficient and economical conversion of flue gas CO₂ to green butanol.

Enhancing CO₂ adsorption on the 3DG surface improves the density and speed of charge transfer between the CuP₂ catalyst and CO₂ to achieve a stable electrocatalytic conversion. We propose the following activities to demonstrate the production of green butanol fuel from CO₂:

1. Develop 3DG for CO₂ reduction using alkali-metal chemistry.
2. Characterize size-confined CuP₂ nanoclusters in 3DG.
3. Accelerate CO₂ electrochemical activation at the interface reaction.
4. Conduct life cycle assessments (LCA) of the process.
5. Simulate the CO₂ electrochemical catalytic reduction.

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, butanol is one of the best replacements for fossil fuels. Minnesota is one of the pioneering states in the US for promoting green alternative fuels such as ethanol and butanol, especially since butanol can be a direct substitution for fossil fuel-based gasoline. Removing CO₂ from industrial sources or the atmosphere, coupled with cutbacks in fossil fuel use effectively relieves the dual pressures on Minnesota's environment and resources.

Activities and Milestones

Activity 1: Develop 3DG and nitrogen-doped 3DG with selected features from the reduction of CO₂ via the alkali-metal chemistry-based strategy

Activity Budget: \$57,824

Activity Description:

Since graphene should have large surfaces for charge accumulation, hierarchical pore structures for transferring electrolyte ions, and continuous 3D frameworks for electron transportation, we will synthesize structured 3D graphene (3DG) by reacting CO₂ with alkaline metals (Na, K, Mg) for novel morphologies, enhanced surfaces, and optimal pore structures using temperature and reaction time controls. This eliminates complicated graphene exfoliation, self-assembly, and surface activation perforation, resulting in 3DG with commercially-desirable morphologies and self-supporting structures for Cu₂P nanocluster catalysts.

Nitrogen doping by heat treatment places graphene derivatives in a tube furnace using nitrogen/ammonia as sources. Compared with non-metal heteroatoms, nitrogen's size is close to carbon and more compatible with graphene's lattice structures. Hence, nitrogen can be more easily doped into the lattices, producing a more stable 3D nitrogen-doped graphene (3DNG). The lattice-nitrogen, compared with carbon, will have one more electron that can enter the conduction band and open the graphene bandgap, thereby obtaining an n-type nitrogen-doped graphene (N-graphene, NG) semiconductor. Nitrogen doping can generate active regions in the graphene lattice and improve CO₂ catalytic reduction performance. The presence of nitrogen is also conducive to the attachment and fixation of metal/metal oxide nanoparticles, preventing desorption from the graphene surface or agglomeration.

Activity Milestones:

Description	Approximate Completion Date
Fabricate 3DG with high surface area, porous structure, and nitrogen doping.	December 31, 2024
Evaluate the structure, composition, and support of 3DG and 3DNG for converting CO ₂ to butanol.	June 30, 2025

Activity 2: Grow size-confined Cu₂P nanoclusters in 3DG frameworks and identify their catalytic applications.

Activity Budget: \$57,823

Activity Description:

Our goal is to develop an in-depth understanding of the precise synthesis and regulation of Cu₂P nanocluster (NC) active centers and reveal the dynamic evolution mechanism of NCs.

NCs with sizes ranging from a dozen to a few hundred atoms hold potential in catalysis due to their unique geometric and electronic structures compared to conventional catalysts. 3DG has a controllable pore structure, high specific surface area, and excellent conductivity for supporting a catalyst. The encapsulation of Cu₂P nanoclusters with sizes ranging from several to tens of atoms in 3DG exhibits high activity and conductivity for CO₂ conversion. We will adopt the direct reaction of active alkali metals and CO₂ to prepare 3DG with the unique surface microporous structure at a low cost, further growing size-confined Cu₂P nanoclusters in graphene frameworks. Then, various characterization methods will determine the crystal phase, crystal type, structure morphology, composition, specific surface area, and CO₂ adsorption capacity. We will also evaluate the electric catalytic reduction of flue gas CO₂ to produce butanol products. Further adjustments will be made to optimize the material synthesis method based on the obtained characterization and results of the performance tests.

Activity Milestones:

Description	Approximate Completion Date
Prepare a 3DG-supported CuP2 NC composite catalyst.	December 31, 2024
Evaluate the electrocatalytic effect of the catalyst.	June 30, 2025
Summarize the structure-activity relationship between the microstructure and the electrocatalytic performance of CuP2/3DG composite materials.	December 31, 2025

Activity 3: Promote electrochemical activation of CO₂ and accelerate the reaction at the electrochemical interface.

Activity Budget: \$57,823

Activity Description:

Since butanol can be separated in the continuous reactor under heating, electrocatalysis should also be coupled with photo- and thermo-catalysis to achieve considerable reaction conversion and rates. The synergistic effect of CO₂ electrochemistry activation and thermal field should promote high catalytic performance and improve the economic viability of the catalytic conversion.

Solid oxide electrolysis cells (SOEC) provide a reaction platform to convert CO₂ into chemical substances through thermally-coupled electrocatalysis, as demonstrated in the oxygen ion conductive electrolyte membrane SOEC. Under the effect of heat coupling electrocatalysis, the thermo-coupled catalytic electrolytic cell will be used to explore the promotion mechanism of the heat-electricity synergistic catalytic conversion of CO₂ through complementary kinetic energy. The ideal strategy for converting CO₂ into high-value butanol products uses SOEC with a proton-conducting electrolyte membrane at moderate temperatures (100-300°C). Thus, we will apply the previously-synthesized advanced catalysts to build a robust electrochemical interface to promote C-C coupling and increase the selectivity of CO₂ conversion to butanol products, while simultaneously inhibiting carbon deposition. We will also study the surface and interface microstructure of electrode catalysts and use a variable temperature reactor to explore the impact of temperature on catalysis.

Activity Milestones:

Description	Approximate Completion Date
Design and optimize SOEC; reliability testing.	December 31, 2024
Investigate the effect of temperature on the electrocatalytic reduction of CO ₂ .	December 31, 2025
Summarize the design strategies of the SOEC and the electro-thermal coupling mechanism.	June 30, 2026

Activity 4: Conduct a preliminary life cycle assessment (LCA) of the new CO₂ capture system to determine potential environmental impacts.

Activity Budget: \$26,530

Activity Description:

A preliminary life cycle assessment (LCA) will be conducted to determine the potential life cycle environmental impacts of the new CO₂ capture system. The LCA will be modeled using SimaPro v9.1.1 software. 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 CO₂ captured or mass/volume of butanol produced). 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 CO₂ capture experiments. Secondary data will be collected from peer-reviewed literature, subject matter experts, and established LCI databases, including DATASmart and Ecoinvent

v3.6. Environmental impacts will be assessed using the LTS Method, which translates the LCI data into environmental impacts on 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	Approximate Completion Date
Complete life cycle inventory of the CO2 capture process.	December 31, 2024
Build an LCA model of the CO2 capture process.	December 31, 2025
Conduct a life cycle impact assessment to determine potential environmental impacts of the process.	June 30, 2026

Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
Richard Davis	University of Minnesota Duluth	Co-PI	Yes
Matthew Aro	University of Minnesota Duluth	Co-PI leading life cycle assessment (LCA) modeling	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 work be funded?

Research into butanol production from CO₂ has received worldwide attention. 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 substantial financial support from governmental agencies (such as the US Department of Energy) and commercial enterprises. The proposed project has also gained support from collaborators, including Dr. Richard Davis and Mr. Matthew Aro, both from UMD. The PI is also willing to support the long-term implementation of this technology using his UMD startup funds.

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 30 high-quality journals, such as Nano Energy and Nature Communications. In addition, he developed several complex chemical process systems to capture CO₂ from a variety contaminated sources. With his strong background in CO₂ capture and conversion processes, the he has the experience to achieve excellent performance in the proposed project and has the capacity and resources to execute this research work at UM-Duluth.

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			27%	0.1		\$16,559
Richard Davis		Co-PI			27%	0.08		\$22,364
Matthew Aro		Co-PI			27%	0.22		\$23,962
Postdoc		Postdoc			20.4%	1.64		\$121,080
							Sub Total	\$183,965
Contracts and Services								
Characterization facility in Duluth or UMN	Internal services or fees (uncommon)	Material characterization fees				0		\$3,500
							Sub Total	\$3,500
Equipment, Tools, and Supplies								
	Tools and Supplies	Lab supplies and Chemicals	consumable lab supplies and chemicals will be used to operate the proposed project					\$9,967
	Tools and Supplies	Life Cycle Analysis software fee	The license is needed to work on the LCA task					\$2,568
							Sub Total	\$12,535
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								
							Sub Total	-
							Grand Total	\$200,000

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request
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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 MTDC project costs of \$200000	Secured	\$110,000
			Non State Sub Total	\$110,000
			Funds Total	\$110,000

Attachments

Required Attachments

Visual Component

File: [6941ba7b-b47.pdf](#)

Alternate Text for Visual Component

CO2 emissions from fossil fuel combustion power plants in Minnesota will be efficiently captured and converted to butanol to help Minnesota reach its greenhouse gas (GHG) emission targets and reduce GHG's negative impacts on the climate....

Optional Attachments

Support Letter, Photos, Media, Other

Title	File
Supporting Letter	419e7fb4-8a0.pdf
UMN Authorization Letter	0c5046d1-36f.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

Does your project include the design, construction, or renovation of a building, trail, campground, or other capital asset costing \$10,000 or more?

No

Do you propose using an appropriation from the Environment and Natural Resources Trust Fund to conduct a project that provides children's services, as defined in Minnesota Statutes section 299C.61 Subd.7?

No