Environment and Natural Resources Trust Fund
2018 Request for Proposals (RFP)

Project Title: **ENRTF ID: 167-E**

Electrically Switchable Adsorption of PAHs on Renewable Cellulosic Nano Carbon Materials for Mitig

Category: E. Air Quality, Climate Change, and Renewable Energy

Total Project Budget: $ 202,000

Proposed Project Time Period for the Funding Requested: 2 years, July 2018 to June 2020

Summary:

A unique nano carbon materials from cellulosic fibers will be examined for adsorption of PAHs, providing an efficient means for mitigation of airborne contaminants at sites of emission.

Name: Ping Wang

Sponsoring Organization: U of MN

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Location

Region: Statewide

County Name: Statewide

City / Township:

Alternate Text for Visual:

Hierarchical carbonized cellulose fiber-carbon nanotube (CC-CNT) materials for electrically switchable adsorption of PAHS

_____ Funding Priorities _____ Multiple Benefits _____ Outcomes _____ Knowledge Base

_____ Extent of Impact _____ Innovation _____ Scientific/Tech Basis _____ Urgency

_____ Capacity Readiness _____ Leverage _______ TOTAL ______%

PROJECT TITLE: Electrically Switchable Adsorption of PAHs on Renewable Cellulosic Nano Carbon Materials for Mitigation of Airborne Pollutants

I. PROJECT STATEMENT

PAHs (Polycyclic Aromatic Hydrocarbons) are increasingly concerned for respiratory health issues including irritation and lung cancer. People can be exposed to airborne PAHs from site-specific sources like tobacco smoke, wood smoke, and smoke from prescribed burning sites, or human activities in more open environment such as vehicles and construction of asphalt roads. Most PAH contaminants are generally products of incomplete combustion reactions that are well distributed in urban and rural communities, consisting over 100 chemical species of varying size and compositions (up to 6 benzene rings fused together). Indeed, 4 of the top 10 most hazardous chemical substances are PAHs according to the 2011 ATSDR Priority List of Hazardous Substances. Minnesota Pollution Control Agency has actively involved in monitoring PAHs emission in the state, however, there is no effective measures and technologies available for mitigation of airborne PAH contaminations (https://www.pca.state.mn.us/air/air-monitoring-polycyclic-aromatic-hydrocarbons-urban-and-rural-sites).

The overall goal of the proposed project is to develop technologies for mitigation of PAHs contaminants for air quality control *in situ* at emission sites. Considering the nature of PAH emission, the technology has to be suited to distributed locations. Specifically we will examine the use of Carbonized Cellulose with surface-patterned carbon nanotubes (CC-CNTs) for selective and intensified adsorption of PAHs. The adsorbed and accumulated PAHs can be recovered and collected from the CC-CNT materials for further treatments (including complete combustion or recycled as waste chemicals). Nano carbon materials offer high specific surface areas, ideal for construction of compact adsorption devices as required for cleaning of PAHs.[1~3] In recent tests for adsorption properties of the hierarchical CC-CNT materials, we observed that highly volatile organic compounds such as ethylene, can be absorbed by the material from a very diluted gas phase (PPM or lower). What is more exciting was that, the adsorption capacity changed greatly when current is applied, with the adsorbed chemicals released quickly from the materials. It implies that the hydrocarbon chemicals can be absorbed firmly and accumulated on the surface of the material under ambient conditions, will then be released and recovered when needed, thereby regenerating the materials for reuse upon application of electricity with high energy efficiency (noteworthy, no detectable temperature changes were observed, mostly due the excellent conductivity of the nano carbon material). We expect such an electrically switchable adsorption/desorption phenomenon can be even more dramatic for PAHs, considering the π-conjugated structures of the molecules that match much better than ethylene to the chemical structures of the nano carbons.

II. PROJECT ACTIVITIES AND OUTCOMES

The electrically-switchable adsorption behaviors of the cellulosic nano carbon materials have been confirmed in our preliminary research. ***In the first year of the project,*** we will examine the adsorption capacity of the PAHs on CC-CNT under different conditions (including temperature and humidity), as well as the electrical current requirements for recovery and collecting the adsorbed PAHs. That will provide essential scientific data for design of the adsorption devices for continuous operations. Model PAH compounds such as benzene, toluene, chloroform and other typical aromatic compounds will be examined through this project. CC-CNT materials will be prepared following procedures as developed previously in the PI's lab,[4,5] with adjustments for control of structural features. The structure of the materials (including content and morphology of the branching out CNTs) will be optimized for PAH adsorption, with specific areas expected to exceed 100 m^2/g. Content of PAHs will be analyzed with GC equipped with an FID detector during the tests. ***In the second year of the project,*** a lab scale continuous adsorption/desorption device in form of packed columns of CC-CNT will be designed and constructed, with which efficiency for air cleaning with model gas mixture samples mimicking real-life air contamination will be evaluated. Operational conditions including temperature and humidity along with specific adsorption capacity will be evaluated, providing basic engineering data for subsequent commercialization of the technology (to be pursued following the completion of the proposed research). Research activities to be conducted through this project will thus examine (1) the adsorption structure-dependent adsorption behaviors of PAHs on CC-CNT, and (2) potentials of the technology for air cleaning treatment. More details of the research activities are provided in the following.

Activity 1: Adsorption Behaviors and Limiting Factors of PAHs on CC-CNT **Budget: $102,000**
Model PAHs including benzene, toluene, chloroform and Dizenzofuran will be examined for adsorption on and recovery from CC-CNT materials; structure of the materials and operational conditions will be examined and optimized accordingly.

Outcome	Completion Date
1. Adsorption capacities and CC-CNT structural optimization	*5 month*
2. Limiting factors (humidity and temperature) for PAH adsorption	*3 month*
3. PAH Recovery Efficiency and Electrical Current Requirements	*4 month*

Activity 2: Lab Scale CC-CNT Adsorption Columns for PAHs Cleaning from Air Flow **Budget: $100,000**
A fibrous adsorption column with electrical desorption/regeneration capabilities will be constructed and examined with continuous air flow mixed with model PAHs contaminants, mimicking real-life air contaminations. Column efficiency will be evaluated in terms of PAH capture, processing capacity and reuse cycles.

Outcome	Completion Date
1. Column adsorption efficiency (theoretical plate numbers and plate height) with different PAHs	*6 months*
2. Effect of impurities and conditions (humidity, temperature and flow rate)	*4 months*
3. Column regeneration and recover of PAHs via electrical current	*2 months*

Expected outcomes and milestone:

We expect the systematic study of the electrically switchable adsorption of PAH species may set forth the fundamentals for development of a new class of technologies for air quality control by mitigating PAH pollution. The proposed research will help to produce preliminary data for more extensive study that eventually lead to the commercialization of the technology, utilizing renewable resources available in Minnesota and improving living quality of both local urban and rural communities.

III. PROJECT STRATEGY

A. Project Team/Partners

The project will be conducted in the PI's lab at UMN. The PI will recruit one graduate student (supported through this project) and 2 or more undergraduate students (work and study plan) for the project.

B. Project Impact and Long-Term Strategy

One major hurdle in applying CNT products is that they are mostly produced in form of powders of CNT bundles, hampering much of the surface areas and properties. The current project promotes the application of a unique hierarchically structured carbonized cellulose- CNT material (CC-CNT), using cellulosic fibers as the raw materials that has been on important forestry product in Minnesota. Long term goals are to develop applications of such materials for broad range of technologies for air quality control and water cleaning.

C. Timeline Requirements

The total duration of the project will be 2 years, with major timelines indicated in the tables above.

References: **[1].**Avouris et al., *Nature Photonics* 2008(2): 341-350; **[2].** Wu et al, *Water research* 2016(88): 492-501; **[3].**Babaa et al., *Surf. Sci*. 2003(531): 86-92; **[4].**Zhao et al., *Bios.Bioelectron*. 2010 (25): 2343-2350; **[5].** Zhao et al., *ACS Appl. Mater. Interface*. 2013(5): 8853-8856.

2018 Detailed Project Budget

Project Title:Cellulosic CNT for Adsorption of PAH's

INSTRUCTIONS AND TEMPLATE (1 PAGE LIMIT)

Attach budget, in MS-EXCEL format, to your "2018 LCCMR Proposal Submission Form".

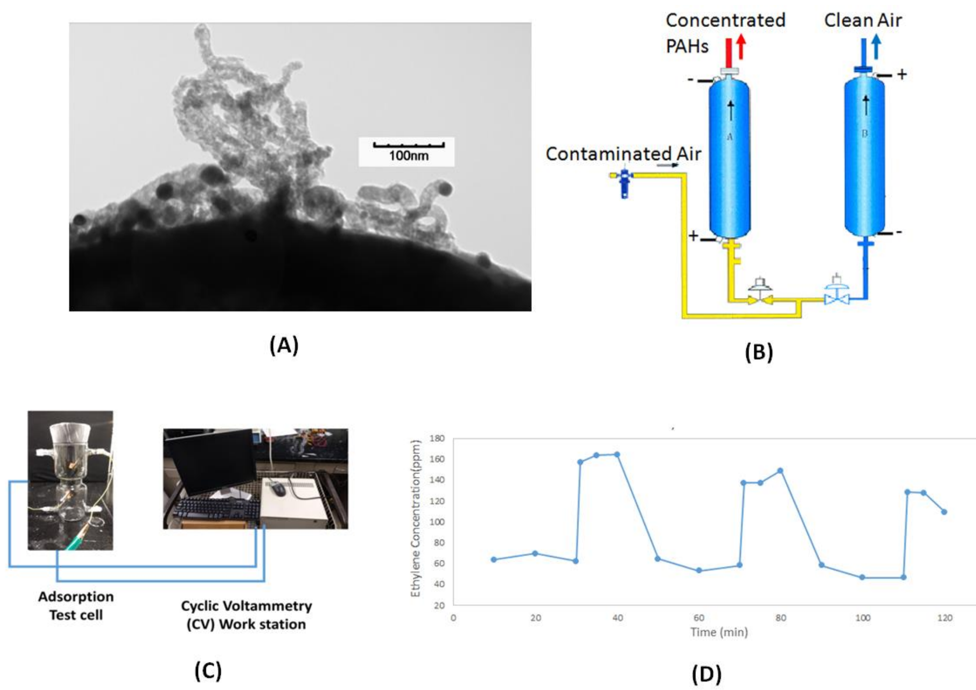
(1-page limit, single-sided, 10 pt. font minimum. Retain bold text and DELETE all instructions typed in italics. ADD OR DELETE ROWS AS NECESSARY. If budget item row is not applicable put "N/A" or delete it. All of "Other Funds" section must be filled out.)

IV. TOTAL ENRTF REQUEST BUDGET *[Two]* **years**

BUDGET ITEM *(See "Guidance on Allowable Expenses", p. 13)*	**AMOUNT**	
Personnel:	$	143,002
Personnel: Ping Wang, PI. Describe responsibilities, (75% salary, 25% fringe benefits) 9 month appointment, summer salary, 13% time	$ 53,070	
1 Graduate Research Assistant, UMN (Twin Cities) Laboratory Experiment Data Analysis (57% salary, 43% benefits); 50% FTE for 2 years each	$ 89,932	
Professional/Technical/Service Contracts: *In this column, list out proposed contracts. Be clear about whom the contract is to be made with and what services will be provided. If a specific contractor is not yet determined, specify the type of contractor sought. List out by contract types/categories - one row per type/category. If an RFP will be issued, state that.*	$	-
Equipment/Tools/Supplies:	$	38,008
Laboratory supplies	$ 38,008	
Acquisition (Fee Title or Permanent Easements): *In this column, indicate proposed number of acres and and name of organization or entity who will hold title.*	$	-
Travel: *Be specific. Generally, only in-state travel essential to completing project activities can be included.*	$	-
Additional Budget Items:	$	20,990
Lab Services: Laboratory analysis	$ 20,990	
TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND $ REQUEST =	$	202,000

V. OTHER FUNDS *(This entire section must be filled out. Do not delete rows. Indicate "N/A" if row is not applicable.)*

SOURCE OF FUNDS	**AMOUNT**	**Status**
Other Non-State $ To Be Applied To Project During Project Period: *Indicate any additional non-state cash dollars secured or applied for to be spent on the project during the funding period. For each individual sum, list out the source of the funds, the amount, and indicate whether the funds are secured or pending approval.*	$ -	*Indicate: Secured or Pending*
Other State $ To Be Applied To Project During Project Period: *Indicate any additional state cash dollars (e.g., bonding, other grants) secured or applied for to be spent on the project during the funding period. For each individual sum, list out the source of the funds, the amount, and indicate whether the funds are secured or pending approval.*	$ -	*Indicate: Secured or Pending*
In-kind Services To Be Applied To Project During Project Period: *Unrecovered indirect costs*	$ 90,957	*Pending*
Past and Current ENRTF Appropriation: *Specify dollar amount and year of appropriation from any current ENRTF appropriation for any directly related project of the project manager or organization that remains unspent or not yet legally obligated at the time of proposal submission. Be as specific as possible. Indicate the status of the funds.*	$ -	Indicate: Unspent? Legally Obligated? Other?
Other Funding History: *Indicate funding secured but to be expended prior to July 1, 2018, for activities directly relevant to this specific funding request. State specific source(s) of funds and dollar amount.*	$ -	



Electrically Switchable Adsorption-Desorption of PAHs with CC-CNT Materials

(A) TEM image of Hierarchical carbonized cellulose-carbon nanotube (CC-CNT), with CNTs branching out from a carbon fiber surface, providing substantially enhanced adsorption capability and unique electrical properties. **(B)** Proposed lab-scale adsorption column devices to be constructed and tested in the proposed research, with both column packed with the CC-CNT materials, column A undergoes desorption to produce concentrated PAHs for collection and further treatment, while column B undergoes adsorption producing clean air; the bi-column design allows continuous operation with adsorption/desorption operations realized alternatively between the two columns with simple electrical switching controls. **(C)** Lab-made bench-top batch adsorption-desorption devices with CC-CNT materials and electrical connections, controlled with a computer station. **(D)** Electrically switchable adsorption and desorption (regeneration) cycle of highly volatile hydrocarbons (ethylene) realized in our preliminary tests, with hydrocarbons quickly adsorbed or released from the surface of the materials (as indicated with low and high concentration of the hydrocarbon in the gas phase of the chamber, respectively) upon application of electronic potentials. We expect PAHs that possess more dense π-electrons will offer stronger binding affinity to the CC-CNT structure.

Ping Wang, PhD

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Qualification Statement: I was educated as a biochemical engineer and have over 20 years of research experience in the area of biotechnology and nanomateirals. The proposed project involves research work on nanomaterials design, chemical adsorption and electrochemical research, areas I have been working through related projects and have generated numbers of publications on each of the subjects out of my over 200 professional publications. The PI's Nanobiotechnology Lab (www.bbe.umn.edu/faculty/pingwang/index.html) is located at the St Paul Campus of University of Minnesota – TC (UMN) and has a lab space of about 1,200 sq feet equipped with fume hood (Rooms 237 and 301), with GC, electrochemical stations and microscopes available for the proposed research. Other analytical equipment (including SEM, TEM, GC-mass, MALDI-TOF and LC-simultaneous ESI and APCI mass spectrometry) are available through the Center for Mass Spectrometry and Micro Image Center (Biodale) that are located in the same building as the PI's lab. Other information about the qualification of the PI is provided in the following.

PROFESSIONAL PREPARATION

B.S., Chemical Engineering, East China University of Science and Technology, China, 7/85
M.S., Chemical Engineering, East China University of Science and Technology, China, 7/88
Ph.D., Chemical Engineering, Tufts University, Medford, Massachusetts, 2/95
Postdoc. Research Associate, Bioprocess/Biocatalysis, Oak Ridge National Lab., 5/97 - 8/99
Postdoc. Research Associate, Biocatalysis/Biopolymers, The University of Iowa, 1/95 - 4/97

PROFESSIONAL EXPERIENCE

Professor, Department of Bioproducts and Biosystems Engineering; Biotechnology Institute, University of Minnesota, 8/09- present

Associate Professor, Department of Bioproducts and Biosystems Engineering; Biotechnology Institute, University of Minnesota, 7/06-7/09

Associate Professor, Department of Chemical and Biomolecular Engineering, The University of Akron, 9/05-6/06

Assistant Professor, Department of Chemical Engineering, The University of Akron, 9/99-8/05

Visiting Scientist, Department of Chemical Engineering, Massachusetts Institute of Technology, 5/90~7/91.

SYNERGISTIC ACTIVITIES

1. ***Editorial Boards***: *Bioengineering and Biotechnology*; *Applied Biochemistry and Biotechnology*
2. ***Meeting Session Organization****:* Session Chair for AIChE and ACS annual meetings, as well as other organizations/occasions such as Biochemical Engineering and Enzyme Engineering Conferences
3. ***Outreach Activities***: Poster and Presentation and Exhibition of Biofuel Cells, USDA Open House of Renewable Energies, Waseca, MN. September 11, 2008; 3r Crop Producer Meetings – Biomass Market, Rural Advantage. Fairmont, MN. Feb. 25, 2008; St Paul Campus Power Puzzle Session, Lego League's Alternative Energy Event for talented high school students at UMN. Oct. 18, 2007.

HONORS AND AWARD:

Outstanding Yang Scholar Award (Abroad), National Science Foundation of China
Outstanding Research Award, College of Engineering, University of Akron, 2006
NSF CAREER Award, 2004