Proposal Title: "Sustainable, High Capacity Graphene Water Filtration at the Molecular Level" for submission to The Grant Challenges Program: Water and Environment Challenge Submitter: Christopher G. Tully, Professor of Physics, Princeton University Date: 03-30-2019

## Abstract:

A single macroscopic molecular layer of carbon in the form of graphene is uniquely the highest flow capacity material for nanoscale desalination and molecular purification of water. The integrity, durability and sustainability of large area graphene will be greatly extended through radio-pure fabrication using thin film metal catalyst carbon dioxide sequestration into methane and subsequent methane cracking into direct graphene fabrication. The proposed method harnesses the large quantities of radio-pure carbon dioxide that are released into the environment as a byproduct of underground digging for natural gas and other fossil fuels. Time is too short to wait for the graphene industry to identify incentives to ramp up production. Water unifies the planet. Starting from an initial system design that was developed to scale to one million sq. meters of graphene, exceeding the current world-wide annual production, and building a stronger collaboration with leading graphene R&D companies, a proof of principle and a viable industrial system can be achieved in two years. We can, with this Grand Challenge, pioneer the technology for sustainable, high capacity water filtration at the molecular level. The funding of this project will seed one of the greatest Earth-saving industrial revolutions of our time.

## Project Description:

Graphene nanosheet and graphene 3D macrostructures (3DMs) have emerged as promising novel membrane material for water and air treatment. Graphene-based membranes can be used for desalination through their natural uniform nanopore structure as well as tailored for the removal of larger contaminants such as dyestuffs, oil and organic solvents, or heavy metals from water. Graphene can be regarded as the 'ultimate' membrane for water treatment, because it is stronger, thinner and more chemical resistant than the classic polyamide active membranes. As the water flux across a membrane is inversely proportional to its thickness, the atomic thinness of graphene produce the highest levels of water permeability. The major obstacles in the realization of a large-scale water filtration system are in the mechanics of supporting the pressure differentials. We will approach this challenge from a new perspective. The goal is to fabricate large-scale freestanding graphene membranes and to seal and support the edges of these membranes through a micro-fabrication process. Novel ultra-high vacuum window structures for X-ray physics with sq. cm surfaces have been achieved with silicon<sup>1</sup>. These micro-fabrication techniques have not been applied to water filtration structures before. Different approaches to fine mesh grids are also possible and enable custom etching to provide different levels of filtration<sup>2</sup>. Graphene nanosheets readily form liquid crystal domains in water to self-assemble 3DMs highly porous and lightweight sponges through hydrothermal or chemical methods, which is a powerful strategy for preserving the high surface area and versatile surface chemistry nanosheets to enhance their environmental performance.

Converting  $CO_2$  into fuel or chemical feedstock compounds could in principle reduce fossil fuel consumption and climate-changing  $CO_2$  emissions. Currently, one strategy aims for electrochemical conversions powered by electricity from renewable sources<sup>3</sup>, while an alternative other approach is the photochemistry driven by sunlight<sup>4</sup>. The electrochemical

conversions are more suitable for large-scale energy processing facilities. The mechanism is the conversion of CO<sub>2</sub> to CO (reverse water-gas shift reaction) followed by CO methanation. CO forms adsorbed carbon species on the catalyst surface, which are subsequently hydrogenated to methane by surface hydrogen. Catalytic activities of metals for CO<sub>2</sub> methanation follow the order Ru> Ni> Co> Fe> Mo with more references here<sup>5</sup>. Considering the high costs of Ru, nickel on a suitable support is a cheap and active alternative. A commercial 18 wt % Ni/Al<sub>2</sub>O<sub>3</sub> catalyst is applied in our work, which has been reported to reaching a production rate 50 L/h methane in a double-jacket tube reactor (V = 452 cm<sup>3</sup>) with 99.9 % methane selectivity<sup>6</sup>. Methane is the main source for current chemical vapor deposition (CVD) graphene growth industry. After CO<sub>2</sub> methanation, the gas chromatography system controls the gaseous mixture of methane and hydrogen with certain ratio to input the graphene growth furnace in the synthesis of large area graphene on Cu foils and graphene nanosheets. The same process of cracking methane to grow graphene nanosheets is also a primary area of development for alternative methods of utilizing the energy stored in methane gas without increasing CO<sub>2</sub> emissions<sup>7</sup>.



This proposal emerged as a great opportunity to join efforts and bring to the forefront the importance of water and the environment with technology challenges faced in fundamental physics research. The underlying concepts on large-scale graphene fabrication presented in this proposal began with a project in neutrino physics, called PTOLEMY, at the Gran Sasso National Laboratory (LNGS) in Italy. The LNGS is a world-leading facility for underground physics, located 1.6km under the Gran Sasso mountain. This mountain is permeable to water and is also the water source for a large population in two neighboring towns, where water quality weighs heavily on the minds of the local residents. The initial system design was conceived to produce one million sq. meters of graphene, exceeding the current world-wide annual production, and a collaboration was started with one of the world's largest graphene R&D companies, Graphenea, in Spain. The graphene industry has not grown at the pace that was expected in the past years. With the urgency and importance of tackling the need to reverse the tide of diminishing fresh water in the world and enabled by the extensive technical capabilities developed at Princeton University by Dr. Fang Zhao at the Andlinger Center cleanroom and PRISM facilities, we propose to dedicate our time on water filtration at the molecular level with graphene and to tackle currently unsolved challenges in the mechanical support of such structures to maintain high flow capacity and durability of the filtration membranes. The high level of fabrication and material science expertise of Dr. Fang Zhao, PhD in Material Science from UCL, can be confirmed with Ian Harvey and the faculty leaders of the Andlinger Center facilities, Prof. Craig Arnold and Prof. Andrew Houck. Dr. Zhao collaborates closely with the groups of Prof. Bruce Koel and Prof. Sanfeng Wu. This proposal will support her salary at half-time for two years and provide funding for the furnaces to conduct this work.

This call is for a great cause for society and one that is of upmost importance to the Gran Sasso community. We believe that this seed funding will generate the momentum that will elevate the Grand Challenge on Water and the Environment to a prominent priority for LNGS and following suit other international physics laboratories around the world, including CERN and Fermilab. A time comes in a scientists' career where one acts the question whether one should dedicate themselves to doing more than just pure academic research. I remember well talking with Prof. Emily Carter at the Big Ideas in Science development office event in Seattle in 2009 about her decision to take on the cause of sustainable energy. I would like to follow in this noble effort and at the same time try to do something good to improve the reputation of the LNGS with the local community and help to raise the importance of water and the environment as a forefront and shared concern for science and the community.

References:

- Huebner, S. et al. High Performance X-ray Transmission Windows Based on Graphenic Carbon. IEEE Transactions on Nuclear Science (2015) Issue 99, <u>http://dx.doi.org/10.1109/TNS.2015.2396116</u>.
- Bassas, H. *et al.* Etching gas-sieving nanopores in single-layer graphene with an angstrom precision for high-performance gas mixture separation. *Sci. Adv.* 5, eaav1851 (2019).
- 3. Parajuli, R. et al. Integration of anodic and cathodic catalysts of Earth-abundant materials for efficient, scalable CO2 reduction. *Top. Catal.* 58, 57–66 (2015).
- 4. Sahara, G. & Ishitani, O. Efficient photocatalysts for CO2 reduction. *Inorg. Chem.* 54, 5096–5104 (2015).
- 5. Mills, G.A.; Steffgen, F.W. Catalytic methanation. *Catal. Rev. Sci. Eng.* 8, 159–210 (1974).
- 6. Methanation of CO2 on Ni/Al2O3 in a Structured Fixed-Bed Reactor—A Scale-Up Study. *Catalysts* **7**, 152 (2017).
- 7. Abánades, A., et al. Experimental analysis of direct thermal methane cracking. *International journal of hydrogen energy* 36.20 (2011): 12877-12886.

## Mentorship:

The physics department has made great strides in increasing diversity through research opportunities and increased individualized attention to providing learning opportunities and experiences that are meaningful to a wider background of individuals seeking to study or participate in physics research. The CBLI program run out of PHY104 by Prof. Tully trained and sent 250+ students into the community to teach at community events, museums, Pre-K and elementary and middle school settings, many in communities with reduced access to STEM education. This last year the Undergraduate Women in Physics (UWiP) was co-founded by Nicole Ozdowski, who worked three summer with Prof. Tully at CERN. This group has made an amazing impact on our community and has been cited positively in undergraduate admissions applications. The LNGS project will provide a compelling opportunity for students to study physics with a cause and opportunities will be provided to work at PRISM and at LNGS to further grow a community of engaged young scientists.