MEMORANDUM OF AGREEMENT
For Sponsored Research

This AGREEMENT is entered into this 1st day of June, 2021 by and between HydroGraph Clean Power, Inc., a corporation having its principal office at #430-580 Hornby Street, Vancouver, B.C. V6C 3B6 (hereinafter referred to as "Sponsor") and Kansas State University, 2 Fairchild Hall, 1601 Vattier St., Manhattan, KS, 66506-1103 (hereinafter referred to as the "University").

WHEREAS, the project contemplated by this Agreement is of mutual interest and benefit to University and to Sponsor and will further instructional and research project objectives of University in a manner consistent with its status as a non-profit, tax-exempt educational institution.

NOW, THEREFORE, the parties hereto agree as follows:

1. STATEMENT OF WORK. The University agrees to use its best efforts to perform the project as described in Appendix A hereof.

2. PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR. The project will be directed by Dr. Chris Sorensen. If, for any reason, he is unable to continue to serve as principal investigator/project director and a mutually acceptable successor is not available, University and/or Sponsor shall have the option to terminate said program in accordance with Clause 15 -TERMINATION.

3. PERIOD OF PERFORMANCE. The project shall be conducted during the period of June 1, 2021 – May 31, 2022 and will be subject to renewal only by mutual agreement of the parties.

4. PROJECT COSTS AND PAYMENT. In consideration of the foregoing, Sponsor will pay University for costs incurred in the performance of the project, without an itemized accounting. All $ amounts are in the currency of the United States of America. Payment shall not exceed the total estimated cost of $1,517,377 USD (not including wiring fees), and shall be payable as per the schedule described in Appendix B.

5. REPORTS/DELIVERABLES. Brief progress reports of the project will be made periodically by University to Sponsor and a final report will be rendered on completion of the project. "Deliverables" mean the report(s) submitted to Sponsor by University which contains the resulting data generated from the project evaluation. The parties agree that Sponsor owns any such Deliverables provided in accordance with this Agreement and Appendix A and thus may use such for any purpose without any further remuneration to University. Notwithstanding the foregoing, the parties understand and agree that University retains the right to (a) utilize the Deliverables for its academic, educational and research purposes, subject to the confidentiality provisions outlined herein, and (b) publish project results as permitted per Clause 12 CONFIDENTIALITY/PUBLICATIONS. During the term of this Agreement, representatives of University will consult and/or meet with representatives of Sponsor to discuss progress and results, as well as on going plans of the project and University will provide project information to Sponsor as reasonably requested.

6. FACILITIES. The University will provide the utilities and office, laboratory and field space needed for the project.

7. PROPERTY. All equipment detailed in the project budget and purchased from this fund shall be the property of the University.

8. PUBLICITY. Sponsor will not use the name of University, nor of any member of University's project staff, in any publicity, advertising, or news release without the prior written approval of an authorized representative of University. University will not use the name of Sponsor, nor any employee of Sponsor, in any publicity, advertising, or news release without the prior written approval of Sponsor.

9. LIABILITY. The Kansas Tort Claims Act (K.S.A. 75-6101 et seq.) sets forth the liability limits of the University as an agency of the State of Kansas for the negligent or wrongful acts or omissions of its employees while acting within the scope of their employment by University.

10. BACKGROUND INTELLECTUAL PROPERTY. "Background Intellectual Property" means property and the legal right therein of either or both parties developed before or independent of this Agreement including inventions, patent applications, patents, copyrights, trademarks, mask works, trade secrets and any information embodying proprietary data such as technical data and computer software. Both parties agree to provide the Background Intellectual Property necessary to complete the objectives of the project. Both parties shall retain all rights to their respective Background Intellectual Property provided for this purpose. Neither party shall assume any rights in the other party's Background Intellectual Property provided for this project other than the right to use said Background Intellectual Property to achieve the objectives of this project.

11. PROJECT INTELLECTUAL PROPERTY. "Project Intellectual Property" means the legal rights relating to inventions (including Subject Inventions as defined in 37 CFR 401), patent applications, patents, copyrights, trademarks, mask works, trade secrets and any other legally protectable information, including computer software, first made or generated during the performance of this Agreement. Ownership of Project Intellectual Property shall vest in the party whose personnel conceived the subject matter and diligently pursued reducing the subject matter to practice, and such party may perfect legal protection therein in its own name and at its own expense. Jointly made or generated Project Intellectual Property shall be jointly owned by the parties unless otherwise agreed in writing.

The parties agree to disclose to each other, in writing, each and every invention which may be patentable or otherwise protectable under the United States Patent laws in Title 35, United States Code. The parties acknowledge that they will disclose inventions to each other and the awarding agency within two (2) months after their respective inventor(s) first disclose the invention in writing to the person(s) responsible for patent matters of the disclosing party. All written disclosures of such inventions shall contain sufficient detail of the invention, identification of any statutory bars, and shall be marked confidential, in accordance with 35 U.S.C. 205.

Sponsor shall receive the first option to negotiate for a license to commercialize the Project Intellectual Property of University, subject to any rights of the Government therein. Sponsor is hereby granted an exclusive option to negotiate the terms for a license to Project Intellectual Property of University, for an initial option period of three (3) months after such invention has been reported to Sponsor.

The terms of subsequent licensing agreements for University owned and/or jointly owned Intellectual Property will be negotiated in good faith and by mutual agreement by the Parties to this Agreement.

12. CONFIDENTIALITY/PUBLICATIONS. During the term of this Agreement, and for a period of five (5) years thereafter, each party will maintain in confidence all confidential Background Intellectual Property and Project Intellectual Property of a party, as well as all other Confidential Information of

a party disclosed by that party to the other in connection with this Project. Neither party will use, disclose or grant use of such Confidential Information except as required to perform under this Agreement. Each party will use at least the same standard of care as it uses to protect its own Confidential Information to insure that students, interns, employees, agents and consultants do not disclose or make any unauthorized use of such Confidential Information. Any student, intern, employee, agent or consultant of the receiving party must be notified of the restrictions on the use of the disclosing party's Confidential Information and must agree with those restrictions before being allowed access to the Confidential Information. Each party will promptly notify the other upon discovery of any unauthorized use or disclosure of the Confidential Information.

Either party may publish its results from this project. However, the publishing party will provide the other party a thirty (30) day period in which to review proposed publications, identify proprietary or confidential information, and submit comments. The publishing party will not publish or otherwise disclose proprietary or confidential Information in accordance with the procedures described in this article and the publishing party will give full consideration to all comments before publication. Furthermore, upon request of the reviewing party, publication will be deferred for up to sixty (60) additional days for preparation and filing of a Patent application which the reviewing party has the right to file or to have filed at its request by the publishing party.

13. MODIFICATION. Any agreement to change the terms of this Agreement in any way shall be valid when the change is made in writing and approved by authorized representatives of the parties hereto.

14. REPRESENTATIVES. Designated representatives for the parties are:

If Technical:

Sponsor:

Harold Charles Davidson
CEO & Director, HydroGraph Clean Power, Inc.
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If Contractual:

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15. TERMINATION. Performance under this Agreement may be terminated by Sponsor upon a thirty day advance, written notice.

Performance may be terminated by University upon a thirty day advance, written notice if circumstances beyond its control preclude continuation of the project. Sponsor's failure to provide funding in accordance with Clause 4 of this Agreement shall be grounds for University to terminate this Agreement, providing such deficiency is not remedied within sixty (60) days of notice by University to Sponsor that, in its view, such deficiency exists.

In the event of early termination of this Agreement by Sponsor or University due to nonpayment of funds by Sponsor according to the schedule in Appendix B, Sponsor shall pay all costs accrued by University as of the date of the notice of termination, including non-cancelable obligations, which shall include all non-cancelable contracts and fellowships or postdoctoral associate appointments called for in Appendix A. In addition, Sponsor will pay all other reasonable costs incurred by the University during the time period between the notification date and the termination date, which are necessary to terminate the project. Any obligation of Sponsor for fellowships or postdoctoral associates shall end no later than the end of University's academic year following termination. Reimbursement for incurred costs and obligations will not exceed the total estimated project cost as shown in Clause 4.

IN WITNESS WHEREOF, the parties have caused the presents to be executed in duplicate as of the day and year first written above.

SPONSOR:	KANSAS STATE UNIVERSITY;
"Harold Charles Davidson"	"Paul R. Lowe"
By: Harold Charles Davidson	By: Paul R. Lowe
Title: CEO, Director	Title: Associate Vice President for Research
Date:	Date: 06/01/2021

APPENDIX A

General Research Plan
Statement of Work
May 20, 2021

I. Process Project. Graphene Production Scale-up. Corkill and Sorensen.

The goal is to create a device that can produce and package graphene at a rapid rate occupying a small foot print that can operate without human attention. A pilot scale device has been built which satisfies the need for the conceptual scheme for the goal. With that foundation, the following issues will be addressed:

Note: the items with possible patentable intellectual concepts are marked *

- * Filtration issues. After the graphene aerosol is emptied from the explosion chamber, it flows into an evacuated collection chamber which collects the bulk of the graphene. However, some of the graphene is still aerosolized and hence flows towards the vacuum pumps. This graphene must be filtered out of the gas phase or else the pumps will suffer. Thus particulate filters are needed.
    - Ongoing tests: Understand filter clogging and determine proper specifications.
    - In operation now: Automated filter blowdown cleaning based on filter differential pressure which detects filter loading.
    - In operation now: flow limiting valve to separate ballast from hopper to slow flow through the filter.
    - In operation now: Isolation for vacuum ballast to reduce lofted particulates.
    - In testing now: Sock pre-filter to limit buildup in filter pleats.
    - Planned: Graphene precipitation tests under vacuum. This will indicate what time and what vacuum level is required for aerosol to fall out of suspension.
- Packaging.
    - Planned: Develop packaging specification and design the system.
    - In operation now: First test of vacuum assisted withdrawal.
        - Original design used inexpensive manual 3” ball valve. This needs to be replaced with actuated version.
    - Ongoing tests: Understand how to prevent caking of samples
    - Planned: Develop shipping specification.
    - Planned: A new hopper design implementing the lessons from the pilot scale device:
        - * The existing system has proven a repose angle greater than 71° is required.
        - The existing vibrator is insufficient.
        - The existing wiping system is insufficient due to existing complications: the hopper is rectangular and has two slopes.
        - The hopper shall be conical.
- * Ignition system. Current system is functioning well but improvements will speed cycle time.
    - desired updates:
        - Started: Pressurized electrode cleaning for faster and more reliable cleaning.
        - Started: Better arc detection.
        - Started: Understand graphene impedance on electrodes to better clean and verify cleaning.

    - Planned: Electrode construction upgrades. Based on developed knowledge design simplified electrodes with increased reliability.
- Vacuum system
  - Solve the continuous issues with pumps and vacuum levels very likely by purchasing top quality pumps (currently, our pumps are either rebuilds or borrowed).
- * Generation 2 system. Based on the above research and testing, design and build modular system for automated mass-production.

II. R&D Canister Project. New Science for New Materials. Sorensen and Bossmann at KSU and Johnson and Fahrenholtz at MST.

Empirical studies. Explore gaseous precursors. Sorensen and Bossmann.

1. Gases with a large Threshold Sooting Index (TSI) such as aromatic hydrocarbons: Benzene, toluene, xylenes, naphthalene, methylnaphthalene.
2. Ethylene, C_2H_4 with oxygen. Mixtures over a broad O/C range, similar to our complete study with acetylene. Depending on results, combinations of C_2H_2 and C_2H_4.
3. H_2 as a minor dopant in C_2H_2 (and possibly C_2H_4) detonations. In a simulation study of our method, a small amount of hydrogen was implicated to have a key role in the graphene synthesis.
4. MAPP gas (propyne-propadiene) which is common and has a large TSI.
5. N_2O as an oxidizer with C_2H_2 (and possibly C_2H_4). N_2O is a good electron quencher.
6. Chamber shape with long length to diameter ratios should effect the shock wave and hence the product.

Theoretical Studies. Understand fundamentals of explosion synthesis. Johnson and Fahrenholtz. Modeling the reaction in the chamber to make graphene. Explain why graphene is formed and not soot.

The empirical studies above will be modeled with hydrodynamic continuum scale simulations. These will be used to predict the temperatures and pressures achieved in the synthesis chamber. Inputs for the simulation can include the size and shape of the reaction chamber as well as the initial composition of the gases introduced into the chamber. The simulation can predict the temperatures, pressures, and durations of the response during reaction including the peak pressure upon ignition (e.g., the Von Neumann spike), the steady-state conditions during reaction (e.g., the Chapman-Jouguet parameters), and the pressure-temperature shock Hugoniot. Temperature-pressure conditions can then be mapped against known pressure-temperature phase diagrams for carbon and other species to determine reaction mechanisms that convert fuel species into the observed reaction products. Simulations will be complemented by and validated using direct measurement of reaction propagation speeds, reaction pressures, and adiabatic temperatures for the reactions studied as part of this project.

Values of pressure and temperature during reaction can also be used as inputs for macroscopic thermodynamic simulations conducted using global Gibbs' free energy minimizations with commercial softward packages such as ThermoCalc or FactSage. These analyses will predict the equilibrium chemical species present under the various conditions as well as the predominant reactions controlling behavior in the system. Heat produced or absorbed by various reactions can be predicted and compared to the overall heat produced (or consumed) by the combustion processes.

The formation of graphene during combustion is likely due to favorable conditions for nucleation of graphite during the combustion wave. Soot typically forms in regimes when combustion products are quenched as they exit a flame. Soot particles grow by addition of gas-phase molecules on nuclei. The rapid combustion process in the confined combustion chamber that we use likely limits the time for growth based on the rapid propagation of the pressure-temperature spike that results from reaction. This hypothesis will be tested by using a combination of the simulation methods with conditions that have known outcomes such as the formation of gaseous reaction products when hydrocarbon-based fuels are combusted in automobile engines or the formation of soot in fuel-rich, ambient pressures.

Goals. What we hoped to be achieve is an understanding of why graphene is formed rather than common soot. With that understanding, we will be able to select precursor materials and conditions to achieve a specific product. Although a precise prediction might be difficult, subsequent iterations will quite likely achieve product goals. A variety of graphenes will allow us to satisfy a variety of product applications. Finally, these studies will lay a strong foundation for attempts to make materials other than carbons via the explosion process.

III. Product Project. Graphene Oxide Development. Bossmann and Sorensen

Upscale GO production to industrial scale (> 1kg G oxidation per batch).

Product. The upscaling process is mandatory for starting graphene oxide production. From the experience of upscaling GO to 200g oxidation batches, we anticipate that the reaction conditions can be adapted to a simple batch reactor. This would have the following advantages: A) The 1kg production unit will be large enough to perform proof-of-concept for much bigger reactors (up to 500kg per batch). B) Performing the reaction in a batch reactor will minimize investment in reactor technology (only unit operations are required (heating/stirring/filtration)).

Process. The technical challenge is not the oxidation, but to obtain a homogenous oxidation product. The general advantage of the GO technology starting from detonation graphene is that the degree of oxidation can be precisely adjusted, leading to tailored surface properties of GO.

Patent In addition/expansion to/of the already existing patent on GO (KSURF PCT/US2020/038055), the process of upscaling defined GO synthesis will be patentable. The hallmark of our GO technology is that the inner graphene layers will remain graphene and only the outer layers and the edges will be oxidized. The total number of stacked graphene layers depends on the graphene production conditions. It is approx. 5 layers for 0.3G and approx. 12 for 0.7 G. FTIR indicates that the surface of GO will be covered with -COOH groups (one per each 4 nm^2). In conclusion, our GO has superior materials properties, because it retains most of the superior properties of graphene.

Synthesize a GO-based Material for the Bike-Industry (Compatible with Epoxy Resins) and other GO-based Materials for Synthesizing Graphene-Polymers.

Product. The underlying paradigm of GO-product development will be that the products will be capable of covalently binding to polymeric materials and resins. For that, we can either modify GO by adding a strong and commercially viable base. The resulting anionic GO will react with oxirane-precursors to form epoxy resins. It will also react with the precursors for PMMA. GO will be molecularly integrated into the resulting polymer network.

The carboxylic acid groups at the surface of GO can be chemically modified by using established bulk-synthesis techniques. For instance, they can be derivatized into alcohols-, esters-, amines, amides, isocyanates, and thioisocyanates. GO reacts effectively with Diels-Alder substrates, thus creating double bonds that can be polymerized via radical and living-chain polymerization reactions. This enables the molecular integration of GO in virtually any polymers, copolymers, and polymer blends.

Patent. The chemistry of molecular connection to polymers will be patentable, because our GO has unique properties.

Synthesize Hydrophilic and Lipophilic G Derivatives without the Need for GO Synthesis (nanobiosensor production, concrete additives, and graphene additives in polymer blends).

Product. The logic behind this approach is that we can save several synthetic steps if we succeed to directly derivatize graphene. For instance, we can attach hydrophobic or hydrophilic side chains by means of carbene or nitrene-addition reactions, which lead to the formation of kinetically stable three-membered rings at the outer layers of stacked detonation graphene. Although these reactions are, principally, published for graphene, they are only published for classic graphene that was obtained from graphite via heavily oxidized classic graphene oxide and reduction of the latter to graphene. With the proposed set of reactions, we achieve this derivatization in a one-step reaction and tailor the surface properties. Furthermore, classic graphene contains many impurities (from graphite oxidation and GO reduction), which may interfere with the proposed chemistry.

Patent. It may be difficult to obtain stand-alone-patents for the proposed G derivatization reactions, because there are some literature reports (albeit not for detonation graphene). However, the materials that can be tailored for multiple applications can be patented as a mandatory component for various materials/applications. For instance, water-soluble graphene will become a component of water-based graphene-inks and printable (super) capacitors.

Test biocompatibility of 10 Surfaces Derived from GO for Biological/medical Applications.

This research will be an initial test of the biocompatibility of GO from detonation graphene. Since our GO is free of toxic metals etc., it should be more biocompatible. Indeed, first cell tests have indicated that this is the case. We envision several future product development endeavors: A) Graphene oxide in medical coatings for instruments and surfaces. B) Graphene oxide for laser-induced hyperthermia experiments, and C) Graphene oxide in Point-of-Care-Detection.

IV. Product project. Graphene/graphene oxide Augmented Materials. Nepal, Sorensen and Bossmann.

1. Composite materials. Polymers and carbon fibers. Hopefully work with Stanley.
2. Concrete (with Prof. Jones)
3. Lubrication.

We have invented, patented and scaled up the detonation technique of making graphene. Now, we believe, it is urgent to determine best match applications for detonation graphene. To date, we have tested nanometer sized graphene platelets as additives to make the following composites:

1. Lubrication oil. Detonation graphene added base oil, an industrial standard, outperformed the pure base oil by ~ 20%. We hypothesize the “spring nature” of crumpled graphene aggregates leads to the application as lubricants.
2. Polymer blends. Detonation graphene added with polypropylene was ~30% stronger than pure polypropylene. Stanley Rokecki implied similar results regarding his bazalt rebar two years ago.
3. Graphene augmented concrete. Current work with Professor **Christopher Jones**, KSU Civil Engineering and concrete expert, is finding detonation graphene added to concrete is ~ 20% stronger than control concrete. This work is in progress.

These positive results for application of detonation graphene mandate systematic studies to find the optimum formulations. Moreover, the most efficient graphene dispersion technique and the best mix proportion of detonation graphene to fabricate composites are to be determined.

These positive results are due to physical mixing with graphene. Chemical mixing, in which strong chemical bonds occur between the graphene and the surrounding matrix, will likely yield greatly enhanced properties for augmented materials. Thus, we also need to explore the application of our unique core/shell graphene oxide (GO), especially for augmenting the strength of materials as in Nos. 2 and 3, above. The carboxylate acid groups on the surface of our GO will allow for controlled chemical bonding to polymers and calcium silicates for these applications while retaining strong graphene cores.

Patent and Product Opportunities. Patents could arise from unique, unprecedented formulations in all three areas. Our graphene oxide is unique. Taking advantage of chemical bonding in Nos. 2 and 3 should make our formulations superior to others.

V. Process Project. Syngas/H2. Engineer No. 2 and Sorensen.

1. As by-product of graphene synthesis
2. From methane/natural gas
3. From LP gas

We have shown that electric spark explosion of fuel rich mixtures of methane, CH_4, and oxygen, O_2, in a multi-liter chamber yields hydrogen rich syngas with a molar ratio of H2/CO $\simeq 1.5$. The method is exothermic; hence, it can produce mechanical energy from the heat. Very little carbon to no carbon is produced. The method converts a severe greenhouse gas, methane, which is by some measures 30 times more potent than CO_2 for global warming, to syngas with a minimal amount of CO_2 by-product. A patent application for this method, "PROCESS FOR SYNTHESIS OF SYNGAS COMPONENTS" by Sorensen et al., Kansas State University Patent Disclosure No. 2021-027 was filed March 16, 2021.

In the next year, we propose the following studies:

1. Use air instead of oxygen to produce syngas by the same method as when using O2.
2. Engineer a rapid filling explosion chamber using an externally driven piston that withdraws to fill the chamber with the CH4/O2 mixture, and then, after explosion, pushes the syngas out for rapid syngas production rates.
3. Develop a continuous process, rather than the current batch method. This will be attempted in the following ways:
    a. Use an off-the-shelf internal combustion, piston engine designed for methane (natural gas) stoichiometric combustion. We will run the engine sub-stoichiometrically, i.e. fuel rich.
    b. Use an off-the-shelf internal combustion, rotary engine. We will run the engine sub-stoichiometrically, i.e. fuel rich.
    c. Study premixed combustion, fuel rich, to determine if syngas can be produced this way.
    d. Build and test turbine and ramjet combustion devices to determine if syngas can be produced this way.
4. Light saturated hydrocarbons such as propane and LP gases that are cheap and industrially available will be tested to determine if syngas can be produced with them.
5. Commercially available gas separation and collection system will be explored and tested.

Patent(s) might be possible for:

1. The complete continuous system that takes the hydrocarbon, converts it to syngas, separates the CO and H2, removes minor impurities, e.g. CO2 and carbon particles, and then stores these gases. However, not that using an engine burning light hydrocarbons to create syngas for methanol production has some old prior art.
2. If we build a small device for "gas stations" with on-sight H2 production for H2 power vehicles, that might be patentable.

This new process is superior to old processes

Currently, 48% of hydrogen production is via the classic steam reforming of natural gas, 30% via oxidation of heavy petroleum and 18% via coal gasification. These methods combined represent nearly 96% of all hydrogen production and all are very endothermic. The source of energy for these methods is predominantly fossil fuels. Consequently, these methods release about 830 million tons of carbon dioxide per year, equivalent to 2.3% of the total worldwide carbon footprint. Because of this, there is significant research and significant funding to find alternate methods or green energy sources to make hydrogen at the industrial scale. For example, the European Union with its Green Deal plan is committed to eventually produce 1 million metric tons of green hydrogen per year [6]. Some of this plan involves renewable wind and solar energy for steam reforming and electrolysis of water. Currently, electrolysis supplies 4% of the world's supply of hydrogen, but it is expensive, and still heavily linked to the combustion of fossil fuels.

Our exothermic explosion synthesis of syngas/hydrogen is a dramatic and viable alternative to these previous methods and has the promise to completely replace them.

Cost Analysis. According to the US Energy Information Administration the industrial price of natural gas ranged from \$3.66 to \$2.72 per 1000 cubic feet from January to June 2020[7]. With these prices, we take an average of \$3.00. We combine this with our demonstrated range of production molar ratios of $H_2/CH_4 = 1.06$ to 1.51 and find our method can yield H_2 at a price of \$0.86 to \$1.23 per kilogram.

VI. Product Project. Manufacturing of functional nano-inks. Das.

1. Understand the surface properties of the materials synthesized via controlled explosion.
2. Nano-ink formulation and scalable manufacturing to beat Ag inks
3. Demonstration of printed energy storage devices using our inks.

The Das group will lead and develop two broad categories of products in this project: functional nano-inks and printed energy storage devices (supercapacitors/batteries). The group has developed two products for its ongoing project (NSF), with a patent (PCT application) currently under review.

In year 1 of this project, we will focus on the expansion of our nano-ink formulation efforts to a wide array of materials synthesized via the controlled explosion method. For example, with **Bossmann and Sorensen**, we will develop graphene/graphene oxide core/shell nano-inks that we expect to **patent** upon development. This will particularly open avenues for developing device architectures for engineered electrochemical energy storage devices. In year 1, we further plan to develop nitrogen-doped graphene ink using a process currently under consideration in our lab. With a number of nano-engineered detonation-graphenes to be developed as described elsewhere in this proposal, we aim to develop a series of nitrogen doped graphene inks for a separate **patent** application. The presence of nitrogen atoms in the graphene lattice significantly enhances the conductivity of graphene. However, nitrogen substitution at specific carbon sites and presence of specific concentration of nitrogen substitution for such optimization will be delivered for the **patent** application. These nano-ink developments will be scaled up by the allocated funding by setting up a lab-scale manufacturing process in the Das lab that will involve a high shear application (> 10^4 s^{-1}) to produce of the order of 500 mL of ink per hour.

In year 2, we aim to design, develop, and scale up printed supercapacitors from the synthesized inks. The primary focus of the project in year 2 will be to target the energy density, cell reliability (in terms of cyclability with high retention, rate capability, and Coulombic efficiency), and structural integrity to benchmark with similar technologies. With the details of device design, fabrication, and operational success, we aim to target a **third patent** application. In a long-term goal, we are interested to explore printed supercapacitors for two different markets – applications where low power and fast charging is needed (using drop-on-demand technology) and those that requires higher power and fast charging (using 3D printed technology).

VII. R&D Canister project. Liquid precursors. Amama and Li.

1. Use fuel injector technology to inject unsaturated liquid hydrocarbons that are difficult to vaporize. This will allow us to explore broadly the parameter space of precursors to find a variety of graphenes to anticipate a variety of applications.
2. Liquids as solvents for novel heteroatoms to yield heteroatom-doped multilayer graphene.

The objective of this task, to be conducted by the **Amama group**, will be to develop the understanding required to design new recipes and processes for controlled explosion synthesis and modification of graphene using liquid hydrocarbons with relatively lower vapor pressures as feedstocks. The use of liquid precursors in explosion synthesis will provide the ability to explore broadly the parameter space of the process, tune graphene properties, broaden the types of nanocarbon materials that can be grown, and anticipate a variety of applications based on the properties of graphene obtained.

The selection of liquid precursors is based on the following properties that are relevant to the growth process: relative stability, ability to control C/O and C/H ratios in the feed, and compatibility with other solvents for doping of graphene with heteroatoms. On the basis of these criteria, the following liquid precursors have been selected: aromatic hydrocarbons (phenol, phenyl alcohols, alky benzenes, and xylenes) and long-chain aliphatic hydrocarbons (higher alcohols). N-doping will be conducted using dimethylformamide in its pure form and as a mixture with the liquid hydrocarbon that shows the highest selectivity towards graphene growth. The objective will be achieved by carrying out a parametric study involving all the feedstocks and establishing correlations between feedstock composition and nanocarbon selectivity.

The morphology, types and quality of nanocarbons produced will be studied by electron microscopy, Raman spectroscopy and thermogravimetric analysis. Spectroscopic techniques will be used to study the composition and local bonding environment and electronic states of the samples after doping. Promising samples will be further probed by transmission electron microscopy with advanced optics to elucidate the morphology and properties of the nanocarbons. The schedule for conducting detonation synthesis and modeling tasks will have significant overlap to allow for an iterative process whereby new mechanistic insights from modeling and growth behaviors observed from material characterization can be further probed during the recipe design.

Products: We expect to not only expand the feedstocks for graphene growth by detonation process, but also improve the ability to tune graphene properties. This study has the potential of providing new and reliable routes for growth of a variety of nanocarbons with exciting properties such as graphyne, graphdiyne, and carbon nanotubes.

Application in Photocatalysis: We anticipate initial application of the graphene samples in our ongoing photocatalysis work (supported by NSF). The work function of graphene is in the range of 4.3 – 5.05 eV, which is more positive than the conduction band (CB) of TiO_2 with a lower work function CB of ca. 4.0 eV. This indicates graphene is energetically well-positioned to receive photogenerated electrons from TiO_2. The formed Schottky barrier enhances charge transfer and separation, which facilitates efficient generation of reactive oxygen species (ROS). ROS in the form of singlet oxygen, superoxide radicals, hydroxy radicals, as well as free electrons can lead to other exciting applications such as bacterial and viral inactivation, wastewater treatment, and air purification.

Patent: Photocatalyst design efforts using semiconductors have focused exclusively on either chemical or bioremediation, even though both pollutants coexist in many environments. This study is expected to lead to fabrication of TiO_2-graphene hybrids that exploit exceptional properties of graphene to address critical limitations of TiO_2. The TiO_2-graphene hybrid films, deposited on common substrates, will offer a new technology platform for building bifunctional photocatalyst coatings with superior activity and durability. The bifunctional photocatalyst, capable of degrading chemical and biological pollutants simultaneously, is expected to exhibit enhanced electron-hole separation and tunable light sensitivity, as well as have a transformative impact on environmental remediation and microbial inactivation. Additionally, the new TiO_2-graphene hybrid is expected to lay a solid foundation for potential adoption of graphene-based hybrid materials in diverse applications including wastewater treatment, surface disinfection, antimicrobial and anticancer therapies, CO_2 reduction, and H_2 generation.

VIII. Catalytic materials and new materials. Amama and Li.

1. Product Project. Heteroatom-doped multilayer graphene as metal-free catalyst and catalyst support.

In this project, **Jun Li's group** will jumpstart using the explosion-produced graphene multilayer as the catalyst support to improve the properties of PtRu catalysts in anode for direct methanol fuel cells (DMFCs). It can be applied to catalytic electrolyzers later. We expect to quickly generate some results that may lead to a **patent application** in a year or so. The key innovations include: (1) Explosion-produced graphene multilayer presents superior electric conductivity and mechanical/chemical stability comparing to the current amorphous carbon support (such as Vulcan or *Ketjen Black* carbon) due to the intact sp^2 graphene structure in the internal stacks; (1) We will extend the Fenton oxidation method developed by Bossmann and Sorensen (patent application pending) to generate oxygenation at the outer layers of the multilayer graphene which promote further deposition of catalysts; (3) We will apply the microwaved-assisted synthesis technique that we developed in an on-going DOE project for improving anode catalysts in DMFCs. We have recently demonstrated significantly higher catalytic properties for methanol oxidation reaction (MOR) in half-cell studies than the state-of-the-art commercial catalysts. This involves an innovative method to deposit a thin-layer of transition metal oxide as the stabilizer for Pt and Ru deposition which enables thermal annealing to form better PtRu nanoparticles at the temperature up to 400°C. Combining the above novelties warrants a **patent application** after we get the preliminary results in a year also. At the meantime, we can study the heteroatom-doped multilayer graphene as the metal-free catalyst alone when the samples are ready.

In the longer term, the catalysts based on multilayer graphene as the catalyst support could be developed as product. MOR is the rate-limiting reaction in DMFCs. The best commercial MOR catalyst is the PtRu catalysts on Vulcan carbon made by Johnson Matthew (JM). Currently, JM only sells it in large quantities to fuel cell manufacturers. If we can provide comparable catalysts at small quantities to research labs, it can already quickly take a **niche market**. In addition, our preliminary data shows that our catalysts have higher performance than the JM catalyst. This allows for use of smaller quantities of noble metal (such as Pt and Ru) which is significant in lowering the cost and make fuel cell technology more competitive than other alternative technologies.

2. **R&D Canister Project. Incorporation of heteroatom dopants such as N, S, P, B and metals into the graphene.**

Noble metal nanoparticles (NPs), such as Pt or Pt group metals (PGM), are the gold standard electrocatalysts for fuel cells, electrolyzers, etc. But they suffer from high cost, limited supply, low selectivity, poor durability and susceptibility to poison. It has been demonstrated that doping carbon nanotubes (CNTs) or graphene with ~ 4-6 atom% of N provided an electrocatalytic activity for the oxygen reduction reaction (ORR) comparable to commercial Pt/C catalysts and they are immune to poisoning by carbon monoxide (CO) and crossover reaction of methanol fuels. Other heteroatoms such as B, S, P and their co-doping with N shows similar effects. The explosion process in principle can effectively produce the heteroatom doped graphene multilayer at low cost by incorporating N-containing gases (such as NH_3 or N_2) or small precursor molecules (such as pyrrole, polyaniline, melamine, etc.). **Jun Li's group** will characterize the at% and atomic configuration of the doping sites, assess the ORR catalytic properties with electrochemistry and help to tune synthesis condition that lead to optimal ORR performance.

In a longer term, metal or metal oxide nanoparticles with organic N-containing precursors can be introduced during explosion. It is notable that, at the high explosion temperature (>2500 ^{o}C), the metal or metal oxide nanoparticles are readily atomized into well-dispersed individual atoms. The quick quenching following detonation may produce dispersed M-N-C single-atom catalysts (SACs). **Jun Li's group** will work closely with **Sorensen and Amama** to address the major challenge, i.e. to find the right conditions to maximize the well dispersed M-N-C SACs and minimize metal particle formation. The fundamental research includes: (i) identifying the optimal conditions for M-N-C formation (such as the type and amount of metal and N precursors, temperature, cooling rate, etc.); (ii) characterizing the obtained structure; (iii) assessing the catalytic activities for ORR; (iv) correlating the metal atoms and heteroatom dopants with the electronic structure and catalytic properties; and (v) investigating how additional light heteroatoms such as S and P into M-N-C catalysts affects the binding of ORR intermediates with metal centers. These fundamental studies lead to the necessary scientific foundation to develop new and better catalyst for a **wide range of applications.**

3. **R&D Canister Project. New materials. Explore synthesis of BCN materials**.

The **Amama group** will work with **Bossmann, Li and Sorensen** to explore synthesis of ternary BCN nanomaterials with alternating B and N atoms partially substituted for C atoms in the hexagonal structure of graphene via explosion process. Experimental strategies will include top-down and bottom-up approaches and be based on current understanding of growth of BCN materials using CVD and arc discharge methods. The task will also be guided by new mechanistic insights from modeling studies of the explosion chamber with **Fahrenholtz and Johnson**. We hypothesize that BCN materials and related nanostructures can be formed during explosion synthesis in the presence of controlled amounts of B-O vapor, carbon and nitrogen. The top-down approach will involve doping of pristine nanocarbons (graphene or carbon nanotubes) with B and N atoms generated from boron oxide vapor and nitrogen (or ammonia) in the explosion chamber, respectively. For the bottom-up approach, we will modify the current precursor used for producing graphene to include B and N precursors. Growth of BCN materials will be explored using the following precursors: (1) CH4/N2/B2H6/H2/O2; and (2) melamine diborate (C3H12B2N6O6), a single feedstock that contains B, C, and N and has the potential of simplifying the growth process. The precursors are selected based on their high selectivity toward growth of BCN nanotubes via CVD. Different feed compositions of the precursors will be investigated under favorable reactor conditions graphene or carbon nanotube growth to control the number of layers and compositions of B-C-N sheets/nanotubes.

Products: The explosion processes that will be developed will enable controlled growth of a variety of BCN nanomaterials including doped graphene, doped carbon nanotubes, BN and BCN nanostructures.

This section **VIII Catalytic materials and new materials** is the launch pad to take chamber explosion synthesis to a great many novel materials well beyond carbon graphene.

IX. Additive Manufacturing. Lin

1. Product Project. Continuous Carbon Fiber Reinforced Epoxy with 2D Materials Enhanced Interlayer Bond.

Motivation. Carbon fiber reinforced polymers (CFRPs) made with continuous carbon fiber and thermosetting are almost exclusively applied for wind turbine blades, transportation, and major structures in the airplanes such as Boeing 787 and Airbus A380 owing to their excellent mechanical properties (high strength, stiffness, and toughness), thermal stability, and chemical resistance. CFRPs typically has five to ten-times the stiffness of aluminum (Al) and steel for the same weight. For example, the ribs and supports in the wing of the Airbus A380 are made with CFREs, resulting in a weight saving of 1.5 tons compared to aerospace-grade Al alloy. However, conventional technologies for manufacturing CFRPs have limited ability to produce composites with complicated, near net-shape architectures, thus constraining structural and functional capability in end-use products.

The design freedoms of additive manufacturing (AM) offers singular opportunity to revolutionize existing manufacturing boundaries for CFRPs (e.g., expensive manufacturing processes and long lead time), especially for complex structures. Thermosetting polymers suffer a significant decrease in viscosity before suddenly turning into a solid, which makes it difficult to infuse thermosetting polymers into a fiber structure and cure them promptly into a solid during the AM process. To date, only two AM processes for CFREs, such as called fused filament fabrication (FFF) and dynamic capillary-driven, localized in-plane thermal assisted (LITA) printing, have been reported. Four major microstructure deficiency in FDM process, including (1) non-uniform carbon fiber distribution, (2) low fiber-matrix bonding strength, (3) interlayer voids, and (4) weak interlayer bonding strength, limits the mechanical performance of the additively manufactured parts. The long time (80 seconds for 10 mm) for capillary-driven infusion and curing epoxy in LITA hinders its real application in 3D printing.

Proposed Additive Manufacturing Process. Herein, we propose a novel Laser-assisted laminated object manufacturing (LA-LOM) process to additively manufacture CFREs with fast speed and superior mechanical properties.

In this project, we will conduct systematic study of printing CFRECs with 2D materials enhanced interlayer bond. To study the process dynamics, the temperature distribution at the interlayer boundaries from each experiment will be monitored by embedded sensors. Advanced characterization techniques, including Scanning Electron Microscope (SEM) and 3-Dimensional X-ray Microscope will be used to characterize the interfacial bonding and porosity. Then the additively manufactured parts with representative process phenomena will be investigated using micro-CT to study the porosity ratio. Moreover, we will automatize the printing process.

The mechanical performance, especially for the high temperature performance will be characterized to establish the process-structure-property relation.

Patent Opportunities. Continuous carbon fiber reinforced polymer composites (CFRPCs), exhibiting superior mechanical properties, have emerged as high-performance engineering materials for various industrial applications. Additive manufacturing (AM) of CFRPCs enables production of customized structures of superior mechanical properties at a low cost and it has gained a tremendous popularity. In the present study, a novel AM technique called laser-assisted laminated object manufacturing (LA-LOM) is proposed for producing CFRPCs using prepreg sheets with continuous carbon fiber reinforcement. The interfacial properties of the bonded prepreg sheets are critical for the performance of the additively manufactured CFRPCs. We further introduce graphene as a modifier between the prepreg sheets to improve the mechanical properties of the CFRPCs. It is shown that low porosity (0.38 %), high concentrations of continuous carbon fibers (63 wt. %), and improved interfacial bonding strength contribute to excellent mechanical properties. For the composite structure ([0°]s fiber arrangements), in which 0.5 mg/ml graphene is introduced as interface modifier, the lap shear strength, tensile strength, and tensile modulus are 18 MPa, 2940 MPa, and 170 GPa, respectively, and the flexural strength and modulus are 1310 MPa and 140 GPa, respectively. The tensile strength and modulus outperform all AM produced structures reported in literature, including carbon fiber composites and metals and metal alloys. Meanwhile, the increases are observed in the lap shear strength by 25 %, flexural strength by 10 %, and flexural modulus by 27 %, as well as tensile strength by 7 % and modulus by 6 %, compared to specimens without graphene reinforcement. This composite architecture design, involving laminated continuous carbon fiber reinforced prepreg sheets and graphene-modified interfaces, provides a readily scalable manufacturing method toward excellent properties and this method can be further explored in industrial applications.

2. Product Project. Additive Manufacturing of High Strength, High Toughness Metal-Graphene Composites.

Goal: The ***goal*** of this research project is to additively manufacture high strength, high toughness metal graphene composites. The Laser Powder Bed Fusion (LPBF) process will be used to fabricate the metal-graphene composites. We will achieve fundamental understanding how graphene in melt pool will enable additively manufacture metal-graphene composite with equiaxed grains toward high strength and high toughness.

Motivation: Laser powder bed fusion (LPBF) is the most prevalent metal additive manufacturing (AM) technique owing to its superior capability to manufacture geometrically complex parts. In a typical LPBF, a laser beam scans across a thin layer of metallic powders, and locally melts the powders through to the layer below. Due to the high thermal gradient and cooling rates in LPBF process, highly columnar grains grow along the building directions. The columnar microstructures in metal and metal alloys, including Al alloys, introduce significant anisotropy in mechanical properties, such as yield strength and ductility to fracture. In this regard, equiaxed grains are preferred due to their better mechanical performance.

The state-of-the-art metal AM techniques achieve equiaxed grains by manipulating scanning strategy, introducing nanoparticles to control the solidification conditions, and adding reactive additions. The most popular and effective technique is to introduce nanoparticles in the melting pool during LPBF. The nanoparticles act as nucleation sites for the equiaxed growth. The distribution of nanoparticles in the melting pool are affected by the buoyancy effect, due to lower density of nanoparticles than molten pool, and the Marangoni effect, induced by thermal capillary forces and high cooling rate. The velocity of buoyancy-driven flow is at least one order higher than Marangoni-driven flow, which drive the nanoparticles to float to the surface of the melting pool. This instability leads to the unstable of grain nucleation sites.

A more stable nucleation sites, graphene nanoplatelets, can be used in LPBF for the equiaxed grain growth. However, the commercially available graphene sheets are too expensive to conduct this research. For example, for a batch of LPBF printing, we normally use 1kg metal powders and it requires 20g of graphene if 2 wt.% of graphene are used in the final metal-graphene composite. The capability of mass manufacturing of graphene at Carbon-2D will enable us to conduct the proposed research: laser AM of bulk metal-graphene composite.

Objective: The objective of the research is to test the hypothesis that mechanical properties of LPBF fabricated samples are significantly enhanced through controlling grain size, improving graphene-metal bonding at molecular level, and graphene reinforcement, all of which are functions of the graphene weight ratio and laser energy density. With success, will come **process patent opportunities** for additive manufacturing of high strength, high toughness, metal-graphene composites.

APPENDIX B

Project Funding Schedule

Payable in four (4) quarterly instalments of $600,000, $305,792, $305,792 and $305,792 each (all amounts in USD).

The first instalment of $600,000 due by June. 1st, 2021.

Subsequent instalments will be due in the following quarters (September 1st 2021, December 1st 2021, and March 1st 2022).