I. PROPOSAL NARRATIVE

Abstract. Here is proposed a new technology to use carbon byproducts or waste (soots, petroleum coke ("petcoke"), etc) for structural and energy applications. Since the discovery of the fullerene people focused on a wide range of pristine carbon structures requiring delicate synthesis with compromised efficiencies (mg/h) and limited to no scalability for mass production, hence cost-prohibited. The idea of optimizing the pristine characteristics of highly pure phases aims to maximize its "theoretical" properties. This is perfect for laboratory work but jeopardizes scalability. I know this problem since 1996 when I was pursuing my MSc degree and started using non-pristine carbon materials for structural composites. To my surprise my results are in some cases two orders of magnitude or more above those with nanotubes, fullerene and graphene. I also discovered a green process for mass production of graphene and morphed graphenes. Morphed graphenes have superior mechanical properties to those seen in graphene; particularly elasticity. A morphed graphene phase is metallic and other one is a semi-conductor, which may be the only pure carbon structure known today with bandgap (~0.4eV). Here is proposed the synthesis of carbon materials for industrial applications for civil infrastructures, energy (e.g. batteries) and composites for structural applications.

Introduction. I have worked on carbon reinforced composites for over 20 years. My reinforcements had always been derivates of byproducts (e.g. soots, black carbon, etc.). During all this time I published a few dozens of manuscripts and made a similar number of presentations in international conferences in this field. I become a true expert in non-pristine carbon structures. For instance, while most researchers struggle to produce 1 g of any pristine carbon structure. I can produce today up to hundreds of grams in ~2 hours that is 200 times or more cheaper than some pristine carbon structures. My scalability to kilograms or tons is limited by my current facility; however, I know well how to build a pilot plant with relatively small funding. Furthermore, I developed a unique methodology to produce graphene at room temperature from carbon byproducts, which is the origin of the discovery of two new phases of carbon, known today as morphed graphenes[1,2,3]. My synthesis is merely environmental based on mechanical processing and it is conducted for the most part at room temperature. The only chemicals that may be involved are: water, ethanol, calcium bi-carbonate ($CaHCO_3)_2$) and heavy liquids. None of them are hazardous. The morphed (see Appendix) graphenes are similar to graphene but with extra bonding (crosslink) in the "*c*" direction having outstanding mechanical properties; presumably superior to graphene. Due to my publications in the area of composites, I am identified as a pioneer of fullerene reinforced composites[4]. I demonstrated the feasibility of my products using matrices such as: metals, ceramics, polymers, C-C, bio-polymers, cement, etc[5,1,6,7,8,9]. In most cases my results translate to superior properties to those seen in pristine structures.

This proposal has the intention to pursue new horizons in terms of scalability and to extrapolate the lab-scale work to industrialization. My target components include, but are not limited to: civil-infrastructure, asphalt, concrete, caterpillar truck tires and batteries. The industries involved in those products are construction, oil and gas, mining, automotive, and the renewable energy sector. All those products require large amounts of carbon for true reinforcement that requires to reuse waste or byproducts otherwise carbon is cost prohibited. I propose to identify large sources of soot, carbon black, and petroleum coke (petcoke) in the nation to be used as vast renewable resource. This waste is considered one of the most detrimental materials for the environment and for this reason it can have even negative price. This is a window of opportunity to reach the main goals of this proposal. For example; carbon reinforced cements and concretes are known, yet cost is a limitation. The department of energy made recently a call for proposals to develop scalable techniques to produce graphite from petcoke for batteries and to minimize graphite imports. Here we propose to investigate the most abundant and rather cheap sources of carbon for industrial synthesis and commercialization of graphite, graphene, morphed graphene, etc. for products that are not commodities, but those who generate high return/profit.

Objectives. (*i*) to identify a long term cost-effective and sustainable source of carbon (e.g. petcoke) to produce composite reinforcements and graphite, (*ii*) to develop technological

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routs for cost effective production of graphite, graphene, morphed graphene, fillers, etc. under environmental conditions for structural and energy applications, (*iii*) to attract industrial, state and/or federal government funding.

Approach: there are several components that we would like to produce in this proposal using petcoke and potentially black carbon. One of them is graphite that is identified essential for battery applications. In April of this year the Department of Energy in their solicitation FOA# DE-FOA-0002322, focus on the production of graphite from petcoke. I communicated with the program director and my work is ideal for this or future solicitations of this kind; yet, I need preliminary results. I also have an NDA agreement with Zen Graphene Solutions, Inc. to produce graphene and morphed graphene from natural resources. To synthetize those products I only need physical means (see Appendix) carried at standard conditions.

The density of graphite varies from 1.9-2.3 g/cm^3, and the petcoke's density is between 1.2 and 1.6 g/cm^3. The separation of graphite requires rapid grinding from petcoke using a planetary mill to reduce agglomeration follow by sonication process until the material is well dispersed either on water, alcohol or directly on heavy liquids. Therefore, once we free the graphite from the amorphous and highly porous matter the materials can be post process separately using heavy liquids. Both products will be characterized to demonstrate its nature (e.g. graphitic, amorphous). The lighter product will be used to produced graphene, morphed graphene or used as a filler for composites. In the event that the lighter product requires exfoliation we will use our environmental defoliation process that involves milling and $Ca(HCO_3)_2$. The $Ca(HCO_3)_2$ is integrated within the carbon layers by milling followed by water washing or diluted citric acid to produce multi-layer graphene[10,11]. The material can be sieved to collect the fines (ideally amorphous) that can be milled again to produce graphene,

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and morphed graphene or again used as filler for composites (see Appendix). I own a domestic and the international patent for the milling process to produce graphene, and morphed graphene as well as its use for composites (: US10086539B2 and WO2015148781A1)[12,13].

Outcomes and Time Frame: the outcomes and schedule are included in Table 1.

Outcome	Months					
	1-3	4-6	7-9	10-12	13-15	16-18
Characterization: density, Raman, SEM, BET, XPS, TEM, XRD, etc.	■	■			■	■
Gravimetric separation and milling		■	■	■		
Graphite enrichment			■	■		
Graphene and Morphed graphene synthesis				■	■	
Reports and presentations		■		■		■

Equipment and Facilities: Most of the equipment for the synthesis is already in my laboratory at UH: planetary mill, sonicators, hoods, Raman, weight balances, dryers. Core facility: Scanning and Transmission Electron Microscope (SEM and TEM), X-Ray diffraction (XRD), X-ray Photoemission Spectroscopy (XPS), Brunauer, Emmett and Teller (BET). Some of this equipment is available at Rice University and I am an Adjunct Associate Faculty there allowing me open access to their facilities at internal fees.

Internal and External Funding: No current or previous funding for this research.

Future Proposal Submissions: we recently agreed to work with Zen Graphene Solutions, Inc. to develop fillers for composites. The Department of Energy is looking for the domestic synthesis of graphite using petcoke, this work will allow mw to rapidly submit a proposal to DoE on this area. In my conversations with Dr. R Khrisnamorty and Mr. C. McConnell we already trying to find ways to attract oil and gas company(ies) willing to invest in this project. Other possibilities include NSF, US Army, Navy, F. government.

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Revised 07/14/2020 **NSF BIOGRAPHICAL SKETCH**

NAME: Francisco C. Robles Hernandez

POSITION TITLE & INSTITUTION: Associate Professor - University of Houston

A. PROFESSIONAL PREPARATION

INSTITUTION	LOCATION	MAJOR/AREA OF STUDY	DEGREE (if applicable)	YEAR (YYYY)
University of Windsor	Windsor Canada	Materials Science and Engineering	PhD	2004
Instituto Politécnico Nacionál	Mexico City, Mexico	Metallurgy and Materials Science	M.Sc.	1999
Instituto Politécnico Nacionál	Mexico City, Mexico	Metallurgy	B.Sc	1996

B. APPOINTMENTS

From - To	Position Title, Organization and Location
	Rice University - Materials Science and Nanoengineering
2019 to date	Adjunct Appointment
2018 to date	Visiting Scholar
	University of Houston
2020	Professor (College of Technology, effective 09/2020)
2018 to date	Member of NSF I/UCRC BRAIN University of Houston Site
2017 to date	Adjunct faculty in Electrical and Computer Engineering
2017 to date	Adjunct Faculty in Materials Science and Engineering
2014 to 2020	Associate Professor (College of Technology)
2013 to 2017	Member of the Center of Advanced Materials (CAM)
2009 to 2014	MS Program Coordinator (Technology Department)
2008 to 2014	Assistant Professor (Technology Department)
	Transportation Technology Center Incorporated (TTCI)
2005 - 2008	Principal Investigator/Project Manager
	NSERC/FORD-NEMAK/University of Windsor IRC
2000 - 2004	Research Assistant
	IPN/Centre for Processing of Minerals and Advanced Materials -
1997 - 1999	Research Assistant

C. PRODUCTS

Products Most Closely Related to the Proposed Project

1. F. C. Robles Hernandez‡† and A. Okonkwo§, (University of Houston) and Dr. H. A. Calderon Benavides (Instituto Politécnico Nacionál – ESFM, México), Synthesis of Effective Carbon Nanoreinforcements for Structural Applications, Patent 10,086,539, Date Issued: October 2, 2018.
2. O. Velazquez-Meraz§, J. E. Ledezma-Sillas§, C. Carreño-Gallardo, W. Yang§, N. M. Chaudhari§, H. A. Calderon, I. Rusakova, F. C. Robles Hernandez‡†, J. M. Herrera-Ramirez, Mechanical improvements on bio-polymer matrix composites by addition of morphed graphene, Composite Science and Engineering, 184, 10, 2019 .
3. H. A. Calderon, D. Barber§, A. Okonkwo§, J. Quintero§, F. Alvarez Ramirez, R. Ordoñez Olivares, V. G. Hadjiev, I. Estrada Guel F. C. Robles Hernandez‡†, Enhanced Elastic Behavior of All-Carbon Composites Reinforced by In Situ Synthesized Morphed Graphenes, Carbon, 153, 2019, 657-662.
4. F.C. Robles Hernández‡†, Calderon HA. Nanostructured Al/Al4C3 composites reinforced with graphite or fullerene and manufactured by mechanical milling and spark plasma sintering. Mater Chem Phys.132, 2–3, 815-22, 2012.
5. V. Garibay-Febles, H. A. Calderón, F. C. Robles Herández, M. Umemoto, K. Masuyama and J. G. Cabañas, "Production and Characterization of (Al, Fe)-C (Graphite or Fullerene) Composites Prepared by Mechanical Alloying", Materials and Manufacturing Processes, 15, 4, 2000, 547-567.

Other Significant Products, Whether or Not Related to the Proposed Project

1. H. A. Calderon, A. Okonkwo§, I. Estrada-Guel, V. G, Hadjiev, F. Alvarez- Ramírez, F. C. Robles Hernández‡†, HRTEM Low Dose: The Unfold of the Morphed Graphene, from Amorphous Carbon to Morphen Graphenes, Advanced Structural and Chemical Imaging, 2, 1, 10, 2017.
2. L. X. Liao§, Q. Zhang§, Z. Su§, X. Lu§, D. Wei§, G. Feng§, Q. Yu§, X. Cai§, F.C. Robles Hernandez, S. Baldelli§, J. Bao, High-efficiency Solar Water Splitting by Nanocrystalline CoO Photocatalyst, Nature Nanotechnology, 9, 69-73-2014.
3. Y. Liang§, H. D. Yoo§, Y. Li§, S. Jing§, H. A. Calderon, F. C. Robles Hernandez, L. C. Grabow, Y. Yao, Interlayer-expanded molybdenum disulfide nanocomposites for electrochemical magnesium storage, Nano Letters, 15, 3, 2015, 2194-2202.

D. SYNERGISTIC ACTIVITIES

Manage groups of professionals and technicians of up to 20 or more people.
Approximately 280 publications (including 4 patents (2 provisional), 3 books, 3 book chapters, 4 times invited editor, 90 peer review papers, 25 proceedings, 129 conference participations, 19 industrial reports, etc).
ADVANCED-UH advocate participant.
Reviewer of scientific proposals for NSF, DoE, and 6 international government agencies and approximately 30 scientific journals.
Co-Organizer of the CAMP summer programs to encourage migrants to pursue higher education on STEM fields.

III. REFERENCES

1. Calderon, H. A., Estrada-Guel, I., Alvarez-Ramírez, F., Hadjiev, V. G. & Robles Hernandez, F. C. Morphed graphene nanostructures: Experimental evidence for existence. *Carbon N. Y.* **102**, (2016).
2. Calderon, H. A. *et al.* HRTEM low dose: the unfold of the morphed graphene, from amorphous carbon to morphed graphenes. *Adv. Struct. Chem. Imaging* (2016) doi:10.1186/s40679-016-0024-z.
3. Velazquez-Meraz, O. *et al.* Improvement of physical and mechanical properties on bio-polymer matrix composites using morphed graphene. *Compos. Sci. Technol.* **184**, 107836 (2019).
4. Garibay-Febles, V. *et al.* Production and characterization of (Al, Fe)-C (graphite or fullerene) composites prepared by mechanical alloying. *Mater. Manuf. Process.* **15**, (2000).
5. Jagdale, P. *et al.* Flame retardant effect of nano fillers on polydimethylsiloxane composites. *J. Nanosci. Nanotechnol.* **18**, (2018).
6. Robles Hernández, F. C. & Calderon, H. A. Nanostructured Al/Al4C3 composites reinforced with graphite or fullerene and manufactured by mechanical milling and spark plasma sintering. *Mater. Chem. Phys.* **132**,(2012).
7. Robles-Hernández, F. C. & Calderon, H. A. Synthesis of fullerene by spark plasma sintering and thermomechanical transformation of fullerene into diamond on Fe-C composites. in *Materials Research Society Symposium Proceedings* vol. 1243 (2010).
8. Robles Hernandez, F. C. *et al.* Characterization of all carbon composites reinforced with in situ synthesized carbon nanostructures. in *Materials Research Society Symposium Proceedings* vol. 1611 (2014).
9. Robles-Hernández, F. C. & Calderon, H. A. Nanostructured metal composites reinforced with fullerenes. *JOM* **62**, (2010).
10. Estrada-Guel, I., Robles-Hernandez, F. C., Carreño-Gallardo, C. & Martínez-Sánchez, R. A green method for graphite exfoliation, effect of milling intensity. *Microsc. Microanal.* **20**, (2014).
11. Estrada-Guel, I., Robles-Hernandez, F. C. & Martínez-Sánchez, R. *A green method for graphite exfoliation using a mechanochemical route*. *Materials Characterization* (2015). doi:10.1007/978-3-319-15204-2_18.
12. **F. C. Robles Hernandez**‡† and A. Okonkwo§, (University of Houston) and Dr. H. A. Calderon Benavides (Instituto Politécnico Nacionál – ESFM, México), Synthesis of Effective Carbon Nanoreinforcements for Structural Applications, Patent 10,086,539, Date Issued: October 2, 2018.
13. **F. C. Robles Hernandez**‡† and A. Okonkwo§, (University of Houston) and Dr. H. A. Calderon Benavides (Instituto Politécnico Nacionál – ESFM, México), Synthesis of Effective Carbon Nanoreinforcements for Structural Applications, Patent: WO 2015/148781 Al, Date Issued: March, 2015.

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V. APPENDIX (Optional)

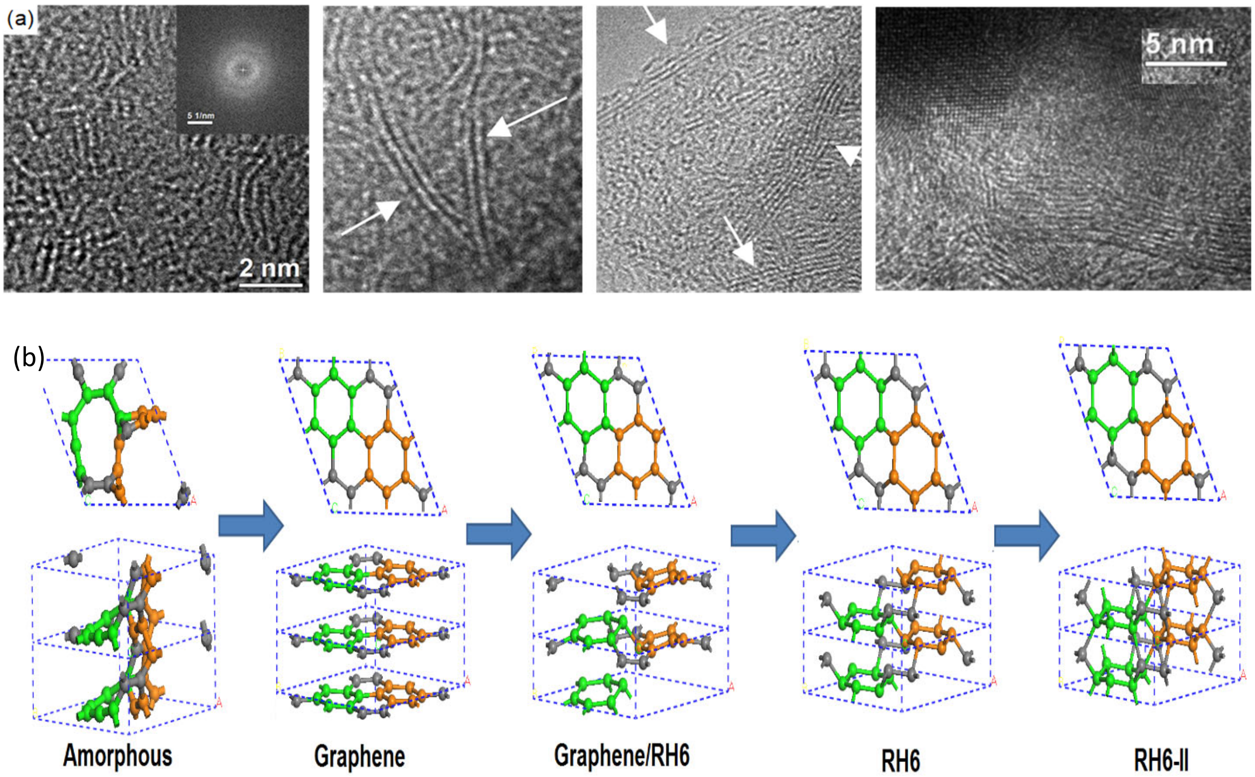

Figure A. (a) Atomic resolution transmission electron microscopy of amorphous carbon and milled carbon demonstrating the presence of double layer graphene, morphed graphene RH6 and morphed graphene type RH6II and (b) simulated structures and synthesis evolution with milling time from amorphous to morphed graphene phases RH6 and RH6-II.

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