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Approved for public release; distribution is unlimited.

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RPPR Final Report
as of 17-Dec-2019

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STEM Degrees: 1 **STEM Participants:** 1

Major Goals: A roll-to-roll plasma manufacturing system will be developed to mass-produce graphene and related nanostructured materials. The system will have direct impact on the increase of the efficiency and performance of nanomaterials and devices. Major goals are:
*A feed rate of 1 km per day production of graphene.
*Mass produce graphene nanopetals for glucose biosensors, supercapacitors and composites.
In this program, several value propositions have been tested by interviewing customers. The market-product fit model is examined to identify the opportunities and to avoid failure. This project will help us to discover customers that are willing to purchase the subject technology as a value-added element to their products.

Accomplishments: Our system is capable of processing several substrates ranging from copper foils to carbon fiber to polymer to plastics. Three main purposes, among others, can be served by our system: growth of graphene layers, graphene nanopetals, and functionalizing of materials. Fisher’s group has demonstrated several applications of plasma processing of different materials that are described below
Application 1. Glucose Biosensors
A glucose biosensor was developed by depositing graphene nanopetals using microwave plasma CVD and then activating the nanopetals edges by platinum (Pt) nanoparticles. This sensor shows excellent characteristics in terms of sensitivity, linear sensing range and detection limit for long usage times. The minimum detection limit achieved with this sensor is 0.3 μM with a linear range of 0.1-50 mM. The biosensor detects current from the oxidation of hydrogen peroxide (H2O2) that reacts with the electrode’s surface. This measured current indicates the concentration of the enzyme glucose oxidase (GOx) since H2O2 is produced from the reaction of water with the glucose.

The graphene nanopetals in this sensor can be made at large scales using our roll-to-roll plasma CVD system. The results of this work will result is a transformation of lab-based biosensors to minimally viable products (so-called “MVPs”) that can address critical issues in the diabetes care market. This sensor has long shelf-life (5 weeks) and so can compete with other commercial glucose sensors in the market.

Application 2. Supercapacitors
The storage of electricity is one of the main challenges with the advent of electric vehicles and renewable energy resources. These storage devices must offer large power density, low weight and fast charging and discharging capabilities. Supercapacitors are one of the promising future power storage devices. In our work, we have demonstrated high performance supercapacitors with capacitance of 2000 F/g, large specific capacitance 2.6 F/cm2 with low current density of 100 A/g. The supercapacitors were made in our small scale microwave plasma

CVD system and have been used to power a light-emitting diode (LED). A conducting polymer, polyaniline (PANI), was used as a substrate material to coat graphene nanopetals and increase their capacitance through supplemental redox reactions.

These graphene-based supercapacitors have power and energy densities that are among the highest ever reported, making them suitable for commercialization. For example, the supercapacitors have 10 times higher energy density than existing commercial supercapacitors (3.5V/25-mF). At the same time, the power density of supercapacitors is two order of magnitudes higher than lithium thin-fi lm batteries.

Application 3. Enhancement of Carbon Fiber Properties
Carbon fibers are the building blocks for many industrial applications due to their light weight and high strength. These applications are found in airplanes, automobiles, wind turbines and construction materials, among others. The strength-to-weight-to-cost ratio is an important factor to consider for competing in these markets. Plasma processing has been used to enhance tensile strength and more importantly increase the bond between the carbon fiber and an epoxy resin commonly used in composites.
We have shown previously the growth of graphene nanopetals on carbon fiber using a plasma CVD system. Using statistical design of experiments techniques, we have optimized the growth of graphene on carbon fibers in a roll-to-roll plasma system. The results show that the surface area of the fiber doubles due to the growth of carbon nanostructures. Also, the electrical resistance of carbon fibers decreases by 50% after plasma processing. These enhanced properties are expected to enable new applications of carbon fibers at lower weight and prices.

Further, in a recent report, we have shown than the thermal interface resistance in carbon fiber/epoxy resins composite drops from 18 to 3 mm2K/W. This increase in the coupling between the carbon fibers and the matrix (epoxy resin) can increase the thermal performance of carbon fiber composites. We assume that similar improvements will be evident in mechanical properties, such as peeling and the shear strength, due to the increase of the surface area and the wettability of the carbon fibers after plasma treatment.

Application 4. Synthesis of Graphene on Metals
Graphene has been shown to prevent oxidation of several metals, such as copper and nickel. Our laboratory work shows that few-layer graphene can be deposited on Cu foil in less than 5 minutes using microwave plasma CVD. Recently, we have worked to increase the quality of graphene with faster processing in the roll-to-roll plasma system. Statistical tools such as design of experiments and multi-objective optimization have been implemented to guide process development. Graphene deposition as a winder speed of 0.8 m/min has been successfully achieved to demonstrate the deposition of one km long graphene on copper foil in less than a day. Copper foil coated with graphene can be used in electrical contact applications (e.g., mobile phone charging/data connectors) and can replace the use of expensive rare-earth materials. Importantly, we have also preliminarily demonstrated the ability to synthesize flat graphene on aluminum – a major advancement given aluminum's low melting temperature.

Training Opportunities: This project supported the completion of the doctoral degree requirements for Dr. Majed Alrefae (PhD, Purdue, May 2018)

Results Dissemination: K.R. Saviers, M.A. Alrefae, T.S. Fisher, "Roll-to-roll production of graphitic petals on carbon fiber tow," Advanced Engineering Materials, Vol. 20, no. 8, art. no. 1800004, 2018.

A. Candadai, A. Kumar, M.A. Alrefae, D. Zemlyanov, T.S. Fisher, "Rapid colorimetric analysis of graphene on copper," Corrosion Science, Vol. 138, pp. 319-325, 2018.

M. Alrefae, A. Kumar, P. Pandit, A. Candadai, I. Bilionis, T.S. Fisher, "Process optimization of graphene growth in a roll-to-roll plasma CVD system," AIP Advances, Vol. 7, 115102-20, 2017.

Honors and Awards: Our plasma-based technologies have created a broad portfolio of technological advances. However, nearly all prospective partners and customers of this graphene portfolio have expressed the need to demonstrate production scalability for the technology to become of high interest. This topic was particularly prevalent in more than 100 interviews with customer prospects through the Spring 2017 NSF/DoD iCorps program (San Diego cohort) in which Fisher, his student Majed Alrefae, and mentor Keith Williams participated. Notably, the student was awarded the only prize of this iCorps cohort as the Most Improved Entrepreneurial Lead.

Protocol Activity Status:

Technology Transfer: Our technologies are highly process-oriented, and as such, the related intellectual property strategy is dominated by the protection of trade secrets rather than published inventions.

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)
Participant: Majed Alrefae
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: PD/PI
Participant: Timothy Scott Fisher
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Consultant
Participant: Keith Williams
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Nothing to report in the uploaded pdf (see accomplishments)