Projects: **1. Energy Storage Devices Based on Three Dimensional (3D) Graphene and Carbon Nanotubes (CNT): Case Supercapacitors and Lithium–Ion Batteries**

2. Electro-chemical Sensors Based on 3D Graphene and Carbon Nanotubes.

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Graduate students will be also involved.

Project Summary Related to Project 1.

The *big idea* for this project is the National Academy of Engineering Grand Challenge to "Make Solar Energy More Economical." The fast development of renewable and sustainable energy techniques such as solar cells and wind turbines requires efficient energy storage systems to offset the fluctuations in power availability caused by clouds or varying winds. The central *challenge* or objective of this project is to develop technology to produce a seamless 3D graphene called a **Graphene Pellet (GP)** and Carbon Nanotube **(CNT)** structure that are synthesized through chemical vapor deposition (**CVD**) using inexpensive nickel powder as catalyst template [1, 2]. GP is an important new platform for fabricating high performance supercapacitors, which is the first application of GP we intend to pursue. GP possesses well-controlled pore size (~2 nm), high electrical conductivity (148 S/cm) and good electromechanical properties. After electrochemical coating with manganese dioxide (**MnO_2**), the GP/MnO_2 electrode shows specific and volumetric capacitance up to 415 F g^{-1} and 235 F cm^{-3}, respectively, with capacitance retention of 90% after 5000 charge-discharge cycles. Moreover, when GP/MnO_2 electrode is assembled with GP/polypyrrole electrode, the fabricated full cell prototype (supercapacitor) shows a superior electrochemical performance with a maximum energy density of 22.3 Wh/kg, maximum power density of 16.4 kW/kg, and very good cycle life that was able to power a light emitting diode (**LED**). These performance characteristics compare favorably to existing supercapacitors.

What work needs to be conducted to achieve the objectives?

This research answers the *guiding question: How do we fabricate multiple supercapacitors and batteries with reproducible properties?* To answer this guiding question, following 6 tasks are proposed to be undertaken:

- Purchase of commercially available housing of supercapacitors and batteries.
- Synthesis of 3D graphene.
- Manufacturing of the positive electrodes of the supercapacitors and batteries.
- Manufacturing of the negative electrodes of the supercapacitors and batteries.
- Assembling the supercapacitor and battery devices.
- Electrochemical testing the supercapacitor and battery devices.

What research facilities will be used to conduct the research?

The Nanoworld Laboratory at University of Cincinnati (http://www.min.uc.edu/nanoworldsmart) will be used for the research projects. It is a College laboratory for material and device development, teaching, and demonstrations. Nanoworld is an internationally recognized laboratory for trailblazing and road mapping innovation, translating the discoveries to industry, and training a next generation workforce that will be in high-demand.

Four labs form the Nanoworld Labs at University of Cincinnati:

- NANOWORLD, Main Lab 414A, 414B & 413 Rhodes Hall, Ph. 513-556-4652
- Nanocomposite Materials and Characterization Labs, Rhodes 507 and Rhodes 506
- Substrates and Nanomaterials Processing Laboratory, 581 Engineering Research Center (ERC)
- Pilot Microfactory for Nanomedicine Devices Lab, 587 ERC

Nanoworld may be the largest nanotube research laboratory in an academic setting with three commercial nanotube reactors to synthesize nanotube materials and transition the processes to industry. Nanotube reactors are in continuous operation along with post-processing and characterization equipment. Magnesium (**Mg**) single crystal manufacturing and coating systems are also used for developing biodegradable implants.

University of Cincinnati Nanoworld supports research for undergraduate and graduate students from across the university. Prof. Vesselin Shanov of the Department of Chemical and Environmental Engineering (**DCEE**) and Prof. Mark Schulz of the Department of Mechanical and Materials Engineering (**DMME**) direct the Nanoworld lab. Faculty members from across the University and from the UC College of Medicine collaborate with Nanoworld.

The main nanotechnology research in Nanoworld is in the field of synthesis, processing and characterization of carbon nanostructured materials, fibers, metal nanowires, nanocomposites, smart structures, electromagnetic devices, and sensors. Nanoworld is also developing innovations in medicine including Mg materials for biodegradable implants, microsensors and devices for interventional cardiology and cancer, and smart biodegradable implants.

Nanoworld is also comprehensively involved in education and is frequently used to host middle school and high school students along with their science teachers. Nanoworld leads teaching two undergraduate nanotechnology courses at University of Cincinnati and one graduate course. These courses use state-of-the-art instrumentation in Nanoworld to perform lab modules. Also, students from other courses tour Nanoworld and learn about nanotechnology, biodegradable metals, biosensors, biomedical devices, and other advanced topics. Undergraduate through Ph.D. students, post-doctoral fellows, faculty members, and industry collaborators all work together in Nanoworld. Hundreds of people visit Nanoworld each year. The faculty members affiliated with Nanoworld bring a great deal of expertise and time to mentoring the students to assure the education and research experience is successful.

Illustration of the current results related to this research project.

Figure 1. displays achievements related to the proposed research, which also have been recently published [1-4].

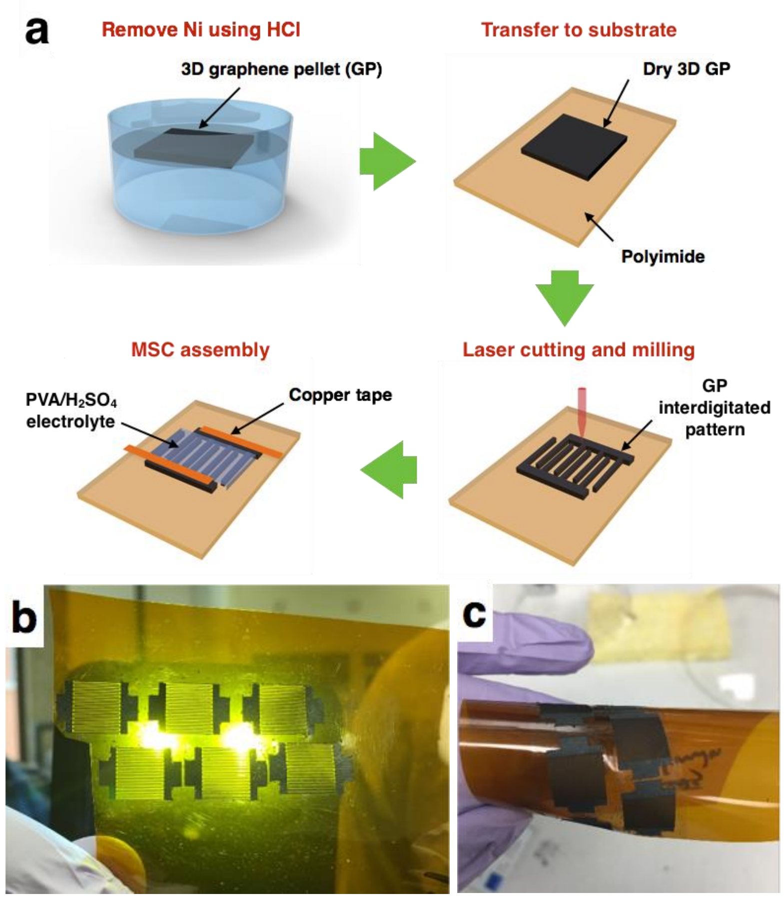

Figure 1: (a) Schematic diagram showing the fabrication process for a GP-MSC. After etching the Ni catalyst with HCl acid, the obtained GP was transferred onto a Kapton (polyimide) film and dried at 50˚ C for 12h. A good adhesion between GP and Kapton substrate was created due to van der Waals forces and the unique morphology of the 3D graphene. Laser engraving was then introduced to form interdigitated pattern, followed by drop-casting a gel electrolyte PVA/H_2SO_4 to complete the GP-MSC. Copper tape was used for interfacing the device with the instrument for electrochemical characterization; **(b, c)** The fabricated multiple GP-MSCs are flexible and can be produced on virtually any substrate of interest.

References

1. Zhang L, Alvarez NT, Zhang M, Haase M, Malik R, Mast D, Shanov V. et al. Preparation and characterization of graphene paper for electromagnetic interference shielding. Carbon. 2015;82:353-9.
2. Shanov V., Zhang L., Alvarez N., Zhang M., DeArmond D., “A Graphene Paper and a Process for Making Graphene Paper and a Graphene with Three Dimensional Structure for High Performance Pseudocapacitor Electrode”, U.S. Provisional Patent Application 62/144922, filed April 09, 2015, based on Invention Disclosure UC 114-036, 02/03/2014 and UC Invention Disclosure, 115-100, 03/26/2015.
3. Zhang L., DeArmond D., Alvarez N., Zhao D., Wang T., Hou G, Malik R., Heineman W., Shanov V., “Beyond Graphene Foam, a New Form of Three-Dimensional Graphene for Supercapacitor Electrode”, J. Materials Chemistry A, 2016; 4: 1876-1886, DOI: 10.1039/C5TA10031C.

4. L. Zhang, D. Armond, N. Alvarez, R. Malik, N. Oslin , Colin McConnell, P. Adusei, V. Shanov, "*Flexible Micro-Supercapacitor based on Graphene with Three Dimensional Structure*", Small, DOI: 10.1002/smll.201603114, pp. 1603114 (2017).

<u>Project Summary Related to Project 2.</u>

Please see the poster below: