

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 (**MnO₂**), the GP/MnO₂ 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/MnO₂ 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].

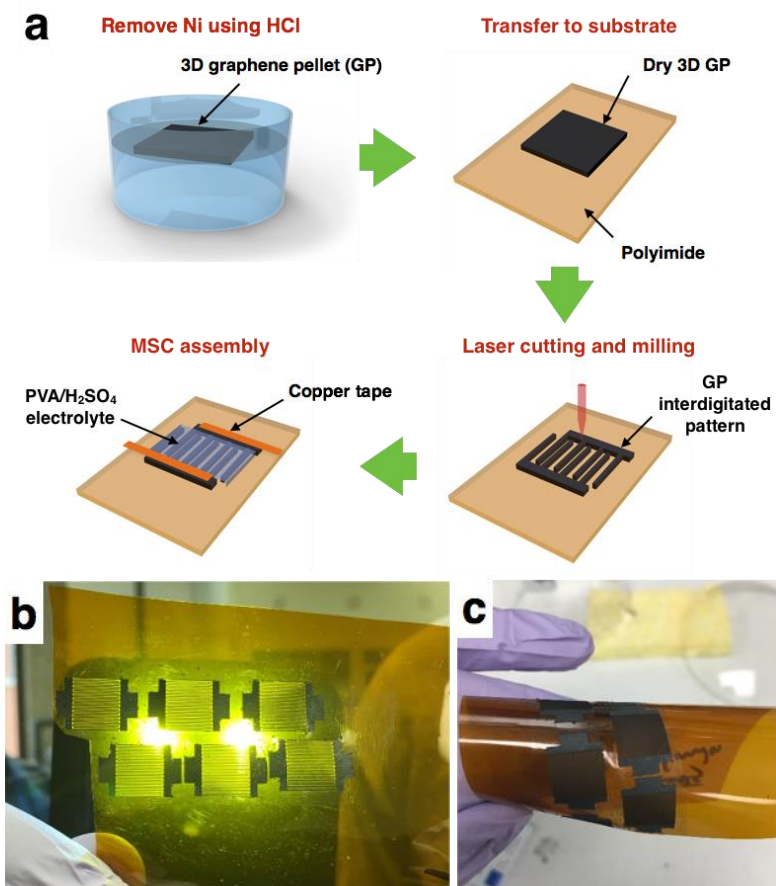


Figure 1: (a) Schematic diagram showing the fabrication process for a GP-MSC. After etching the Ni catalyst with HCl acid, the obtained GP was transferred onto a Kapton (polyimide) film and dried at 50° C for 12h. A good adhesion between GP and Kapton substrate was created due to van der Waals forces 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/H₂SO₄ 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

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Project Summary Related to Project 2.

Please see the poster below:

Biosensors for monitoring cyanotoxins in water

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Introduction

- Harmful Algal Blooms (HABs) produce unfavorable taste, odor, color, and more importantly release cyanotoxins that can be extremely harmful to humans and animals.¹
- The most frequently reported cyanotoxins are microcystins (MCs), a group of cyclic hepatotoxins and microcystin-LR (MC-LR) is the most commonly occurring variant in the US and around the world.²
- Potential hazard of cyanotoxins to human health; USEPA released a 10-day advisory suggesting the limit of 0.3µg/L for kids.³

MC-LR, C₂₆H₃₄N₁₂O₁₂ (L for Leucine and R for Arginine)

- Current methods to detect cyanotoxins in various water matrices require long processing time, sophisticated instruments, complex procedure and high cost.
- A sensitive, specific, and simple method for monitoring MCs is necessary to immediately institute remedial measures to prevent exposure to these toxins.
- Carbon-based nanomaterials such as graphene (GR) and vertical aligned carbon nanotubes (VACNTs) have electrical and physical properties that are desirable for developing novel submicron sized electrochemical sensors.
- Innovative biosensors using GR (current work) and N doped VACNTs (future work) and their preliminary data are promising in MC-LR detection.

Results

1. Cyclic Voltammetry (CV) & Electrochemical Impedance Spectroscopy (EIS)

During functionalization:

↳ Diazonium *in situ* functionalization; in the first cycle, a wide peak at -0.24 V was observed, while during the second cycle, the peak disappeared.

After functionalization:

↳ Nyquist plots for Step 1 (initial), Step 2 (GR-Aryl-COOH) and Step 3 (GR-EDC/NHS and GR-EDC/NHS-MC) of the procedure. After Aryl-COOH groups grafted, charge-transfer resistance (R_c) increased significantly due to the negative surface (COO⁻). 5.0mM Fe(III)/Fe(II) redox-active species in pH 7.4 PBS buffer.

2. Innovative Material - N doped Vertically Aligned Carbon Nanotubes (VACNTs)

↳ SEM image Thin film of VACNTs deposited by plasma enhanced chemical vapor deposition (PECVD) on silicon wafer. The resulting VACNTs are N doped by using ammonia as nitrogen precursor during deposition. This increased the electrical conductivity of the VACNTs. Nitrogen doping has been proved by X-ray Photoelectron Spectroscopy (not shown here)

↳ Typical Raman spectra of N doped VACNTs showing D and G bands along with a small 2D band. The G band is indicative of graphitic carbon whereas D band indicates defects and deposition of amorphous carbon. Higher D peak indicates in-situ N doping of VACNTs.

Biosensors Preparation and Detection Procedure for MC-LR

Step 1: Fabrication

Graphene

Step 2: Functionalization

Electrografted coupling reagents

Step 3: Conjugation of MC-LR

Incubation biomolecules with MC-LR samples

Step 4: Conjugation of biomolecules

Competitive Detection⁴

Graphene *in situ* functionalization

fast, selective and specific functional groups (such as -COOH)

Synthesis and Characterization of 3D Graphene

Synthesis: Nickel powder sintered to form pellets, which were used as catalyst for CVD growth of graphene. The resulting graphene had 3D structure and higher surface area as compared to multilayer graphene.

SEM image shows CVD synthesized graphene with 3D structure. The structure was porous with large surface area per unit volume.

Typical Raman spectra of 3D graphene prepared using Ni pellets. The characteristic peaks G and 2D can be seen⁵. A very low D peak is indicative of higher quality of graphene.

Contact Angle measurements: Pristine 3D Graphene was found to be hydrophobic, but after functionalization hydrophilic tendency was observed. The contact angle reduced to 35 degrees.

Conclusions

- An efficient Faradaic electrochemical impedance biosensor for monitoring MC-LR in sources of drinking water supplies was introduced using 3D graphene synthesized by CVD.
- Cyclic voltammetry revealed well-defined redox peaks in the presence of Fe(III), and functionalization of graphene has been achieved.
- EIS measurements showed electrochemical impedance increased indicating biosensors could detect MC-LR efficiently. This technique is very promising to detect MC-LR in water.
- New sample - N doping added pyridinic, pyrrolic and graphitic N groups on the walls of VACNTs.
- Future work, (i) test the capability of N doped VACNTs screen-printed electrode, (ii) use of aptamers.

References	Acknowledgements
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